

“Janus” calixarenes: double–sided molecular linkers for facile, multi-anchor point, multi-functional, surface modification

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General Information

Commercially available reagents were purchased from Sigma-Aldrich (Gillingham, UK) and used without further purification unless stated otherwise. Anhydrous reactions were performed under a dry nitrogen atmosphere (BOC Gasses) using standard Schlenk-line techniques on a dual manifold vacuum/inert gas line. All glassware was dried in the oven overnight before use. Anhydrous solvents were dried via distillation over either sodium/benzophenone (tetrahydrofuran (THF) and diethyl ether) or calcium hydride (dichloromethane (DCM)) under an inert nitrogen atmosphere, and sparged with nitrogen gas to remove any trace amounts of dissolved oxygen. Water used in aqueous electrochemical reactions was also thoroughly sparged with nitrogen to remove dissolved oxygen prior to use.

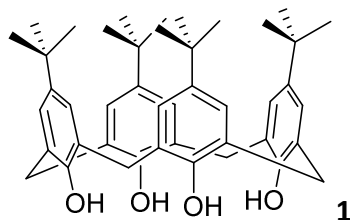
Electrochemical measurements were performed under an inert atmosphere using computer-controlled potentiostat (Model PGSTAT 30, Autolab, Utrecht, The Netherlands) using a standard three-electrode configuration: a glassy carbon electrode (GCE) (BasiTechnicol, diameter 3 mm) served as the working-electrode with a platinum wire counter electrode (99.99%, GoodFellow, Cambridge, U.K.) and either a silver wire quasi-reference electrode (99.99%, GoodFellow, Cambridge, U.K.) or a saturated calomel electrode (Radiometer, Copenhagen, Denmark) used as the reference electrode for non-aqueous and aqueous electrochemical measurements respectively. The working electrode surface was renewed by successive polishing with diamond paste slurries of decreasing particle size ranging from 3.0 μm to 0.1 μm (Kemmet, U.K.). The electrode was sonicated in deionized water and rinsed with ethanol between each polishing step to remove any adhered polishing materials.

Flash chromatography was performed on silica gel (SiO_2 , 70-200 micron mesh 60 Å) purchased from Alfa Aesar. Thin layer chromatograph was performed using silica gel 60 Å F254 pre-coated plates.

Proton NMR (^1H NMR) spectra were recorded using a Bruker Avance DPX-500 MHz spectrometer. The data is reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constant(s) in Hz. Chemical shifts are reported in parts per million (ppm) relative to CDCl_3 (7.26 ppm). Carbon NMR (^{13}C NMR) spectra were recorded at 75 MHz and 125 MHz. Chemical shift is reported in ppm relative to the carbon resonance of CDCl_3 (77.00 ppm). IR spectra were recorded using a PerkinElmer μ -ATR Spectrum II spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific K-alpha instrument using monochromatic Al X-rays. All spectra were corrected relative to the graphitic C_{1s} peak position (284.97 eV).

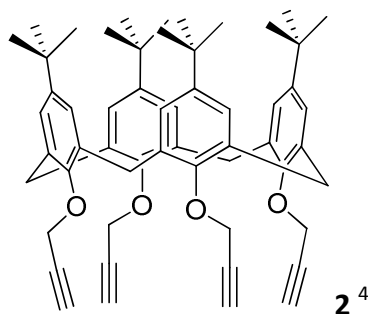
Synthesis of Calix[4]arenes

Synthesis of *cone*-5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene **1**



The preparation of **1** was achieved using a scaled up version of the procedures reported independently by Gutsche, and later of Simaan and Biali.^{1,2} *p*-*tert*-butylphenol (200 g, 1.33 mol) and NaOH (1.20 g, 0.03 mol) were added to a three-necked 3L round bottom flask fitted with an overhead stirrer. The flask was purged with nitrogen, followed by the addition of 37% formaldehyde solution (128 mL, 1.66 mol) and left to stir at 120 °C whilst removing water *via* a right-angled condenser. To the resulting deep-yellow viscous mass that forms, warm diphenyl ether (600 mL, 3.79 mol) is added to dissolve the contents of the flask, and then heated at 110-120 °C to remove water *via* a condenser (a nitrogen stream is required to aid water removal). After all the water has been removed (4-5 hours), the brown solution in the flask is heated to 260 °C for 4 hours. The reaction is then allowed to cool (overnight), to which ethyl acetate (1.5 L, 15.3 mol) is added and the reaction left to stir for 1 hour at room temperature. The resulting beige-solid is filtered off affording **1** as beige powder (95.0 g, 44%). ¹H NMR (500 MHz, CDCl₃): 1.21 (36H, s), 3.49 (4H, d, *J* = 13 Hz), 4.26 (4H, d, *J* = 13 Hz), 7.05 (8H, s), 10.34 (4H, s). ¹³C NMR (125 MHz, CDCl₃): 31.5, 32.8, 34.2, 126.1, 127.8, 144.5, 146.8; IR (neat, ν / cm⁻¹) 3167 (phenol), 2951, 1738, 1481, 1360, 1239, 1200, 1039. (Data matches literature values)³

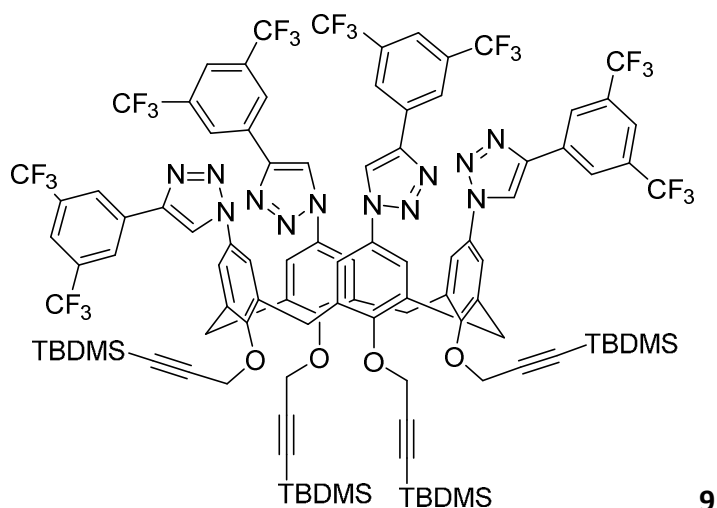
Synthesis of *cone*-5,11,17,23-tetra-*tert*-butyl-25,26,27,28-propargylcalix[4]arene **2**



Following the procedure reported by Chetcuti,⁴ *p*-*tert*-butylcalix-[4]arene **1** (30 g, 46.3 mmol), potassium carbonate (27.2 g, 260 mmol) and propargyl bromide (80 wt% solution in toluene,

33.7 g, 286 mmol) in acetonitrile (1 L) was refluxed for 48 h. The reaction mixture was filtered, and the filtrate evaporated to dryness. Re-dissolving the resulting residue in dichloromethane, followed by trituration with methanol yielded **2** as a cream powder (19.0 g, 51%). ¹H NMR (500 MHz, CDCl₃): 1.08 (36H, s), 2.48 (4H, t, *J* = 2 Hz), 3.16 (4H, d, *J* = 13 Hz), 4.60 (4H, d, *J* = 13 Hz), 4.80 (8H, d, *J* = 3 Hz), 6.79 (8H, s). ¹³C NMR (125 MHz, CDCl₃): 31.5, 32.5, 34.0, 61.2, 74.5, 81.3, 125.1, 134.4, 145.7, 152.5; IR (neat, ν / cm⁻¹): 3295, 2954, 2120 (alkyne), 1745, 1593, 1476, 1362, 1190, 1120, 1017, 1003. (Data matches literature values).⁴

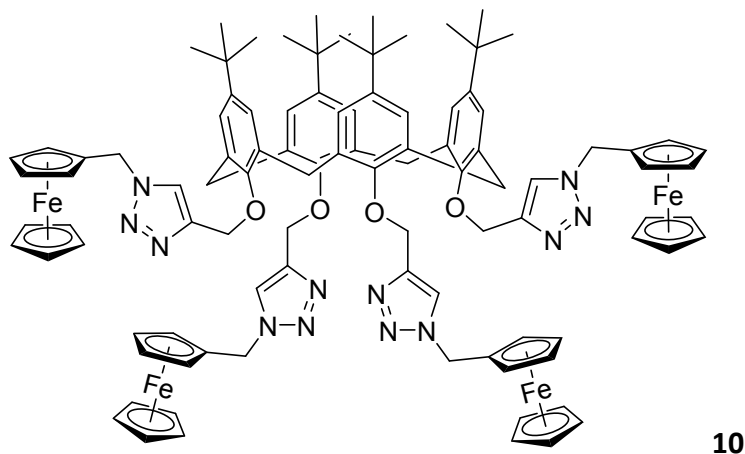
Synthesis of cone-5,11,17,23-tetra-(4-[3,5-bis(trifluoromethyl)benzene]-1H-1,2,3-triazole-1-yl)-25,26,27,28--TBDMS-propargylcalix[4]arene **9**



Cu(SO₄) (82.5 mg, 0.33 mmol) dissolved in 5 mL ethanol:water (1:1) was slowly added to a solution of sodium ascorbate (32.7 mg, 0.17 mmol) in 5 mL ethanol:water (1:1). A separate vessel was charged with calixarene **7** (50 mg, 0.041 mmol) and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (45.3 mg, 0.19 mmol) to which the copper solution was slowly added and the reaction mixture was allowed to stir for 1 hour. Dichloromethane (10 mL) was added and the reaction mixture was rapidly stirred overnight. Once complete, monitored via TLC, the reaction was quenched by the addition of cold water (50 mL), and the product was extracted with dichloromethane (3× 25 mL) washings of the aqueous layer, dried using MgSO₄. The filtrate was concentrated *in vacuo*, and the residue was purified using flash chromatography (acetone/petroleum ether 2:7) to afford **9** as a yellow solid (56 mg, 64%) ¹H NMR (500 MHz, CDCl₃): 0.12 (s, 24H), 0.91 (s, 36H), 3.47 (d, *J* = 13.9 Hz, 4H), 4.82 (d, *J* = 13.9 Hz, 4H), 4.96 (s, 8H), 7.79 (s, 4H), 8.09 (s, 4H), 8.18 (s, 8H). ¹⁹F NMR (471 MHz, CDCl₃): -4.55, 1.17, 16.57, 26.11, 30.96, 32.50, 62.50, 92.31, 100.94, 118.95, 120.73, 121.99, 123.23 (q, *J* = 33.6 Hz), 125.80, 132.22 (q, *J* = 33.6 Hz), 137.24, 145.67, 155.44; IR (neat, ν / cm⁻¹): 2954, 2930, 2869,

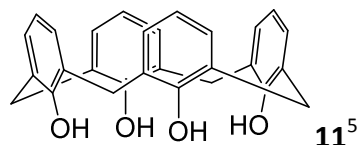
2179 (alkyne), 1596, 1486, 1373, 1277, 1130; HRMS: m/z : $[M + NH_4]^+$ Calcd for $C_{104}H_{104}F_{24}N_{13}O_4Si_4$, 2166.7023, found 2166.7010.

Synthesis of *cone*-5,11,17,23-tetra-*tert*-butyl-25,26,27,28-[(4-methyl-1H-1,2,3-triazole-1-yl)methyleneferroceneylcalix[4]arene **10**



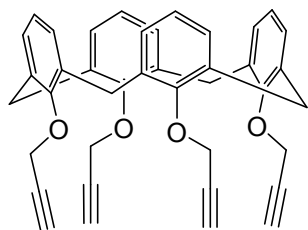
$Cu(SO_4)$ (175 mg, 0.7 mmol) dissolved in 5 mL ethanol:water (1:1) was slowly added to a solution of sodium ascorbate (70 mg, 0.35 mmol) in 5 mL ethanol:water (1:1). A separate vessel was charged with calixarene **2** (69.6 mg, 0.087 mmol) and ferrocenyl methyl azide (45.3 mg, 0.19 mmol) to this the copper solution was slowly added and the reaction mixture was allowed to stir for 1 hour. Dichloromethane (10 mL) was added and the reaction mixture was rapidly stirred overnight. Once complete, as monitored via TLC, the reaction was quenched by the addition of cold water (50 mL), and the product was extracted with dichloromethane (3× 25 mL), dried using $MgSO_4$. The filtrate was concentrated *in vacuo*, and the residue was purified using flash chromatography (acetone/petroleum ether 1:3) to afford **10** as a yellow solid (60 mg, 39%) 1H NMR (500 MHz, $CDCl_3$): 1.03 (s, 36H), 2.72 (d, $J = 11.2$ Hz, 4H), 3.99 (d, $J = 11.2$ Hz, 4H), 4.36 – 4.16 (m, 36H), 4.90 (s, 8H), 5.22 (s, 8H), 6.61 (s, 8H), 7.61 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): 31.45, 31.60, 33.83, 49.89, 66.55, 68.80 – 69.0, 81.94, 123.98, 124.89, 134.07, 144.54, 144.75, 151.95; IR (neat, ν / cm^{-1}): 3094, 2960, 2865, 2243, 1601, 1478, 1462, 1194; HRMS: m/z : $[M + H]^+$ Calcd for $C_{100}H_{109}N_{12}O_4Fe_4$, 1766.6123, found 1766.6096.

Synthesis of cone-5,11,17,23-tetra-H-calix[4]arene **11**



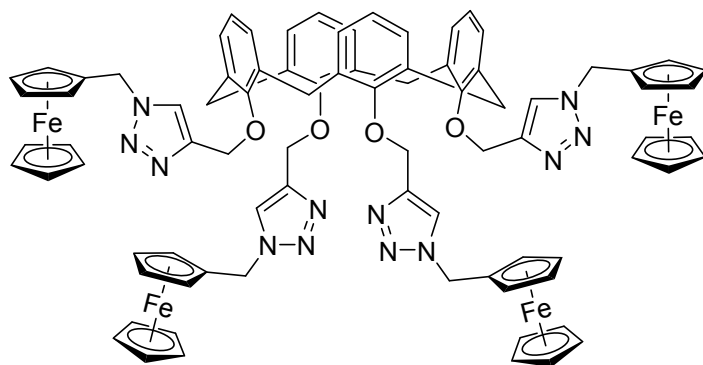
Dry calixarene **1** (10.0 g, 15.1 mmol) was dissolved in dry toluene (200 mL) and heated for 1 hour at 50 °C. Aluminium Trichloride (10.0, 75.0 mmol) was added and the reaction was then stirred for 3 hours, at which point the mixture was cooled to 0 °C and quenched by the addition of 1 M hydrochloric acid (240 mL). The organic layer was separated, washed with water (3 x 100 mL), dried using MgSO₄ and filtered. The filtrate was concentrated *in vacuo* to form a yellow oil followed by trituration with diethyl ether yielded **11** as a light yellow powder (5.0 g, 78%) ¹H NMR (500 MHz, CDCl₃): 3.59 (br, s, 4H), 4.32 (br, s, 4H), 6.78 (t, *J* = 7.6 Hz, 4H), 7.10 (d, *J* = 7.6 Hz, 8H), 10.25 (s, 4H). ¹³C NMR (125 MHz, CDCl₃): 31.05, 31.85, 77.16, 122.39, 129.13, 148.92; IR (neat, ν / cm⁻¹): 3135, 2934, 1594, 1463, 1448, 749, 733.

Synthesis of cone-5,11,17,23-tetra-H-25,26,27,28-propargylcalix[4]arene **12**



Dry calixarene **11** (2 g, 4.7 mmol) and sodium hydride (0.5 g, 20.7 mmol) were dissolved in acetonitrile (40 mL) at 0 °C while stirring. The mixture was allowed to stir for 1 hour before the addition propargyl bromide (80 wt% solution in toluene, 3.0 g, 20.2 mmol), the solution was then warmed to room temperature and the reaction was continued for 48 hours. The reaction was quenched by the addition of cold water (100 mL), and the product was extracted with dichloromethane (3x 50 mL), dried using MgSO₄. The filtrate was concentrated *in vacuo* followed by trituration with methanol yielded **12** as a beige powder (1.2 g, 45 %) ¹H NMR (500 MHz, CDCl₃): 2.47 (t, *J* = 2.4 Hz, 4H), 3.22 (d, *J* = 13.5 Hz, 4H), 4.63 (d, *J* = 13.5 Hz, 4H), 4.78 (d, *J* = 2.4 Hz, 8H), 6.66 (m, 4H), 6.72 (d, *J* = 7.1 Hz, 8H). ¹³C NMR (125 MHz, CDCl₃): 32.03, 61.31, 74.84, , 80.66, 123.41, 128.40, 135.56, 155.16; IR (neat, ν / cm⁻¹): 3279, 2912, 2123, 1585, 1456, 1429, 1199, 1184, 998.

Synthesis of cone-5,11,17,23-tetra-H-25,26,27,28-[(4-methyl-1H-1,2,3-triazole-1-yl)methyleneferreceneylcalix[4]arene **13**



13

Cu(SO₄) (175 mg, 0.7 mmol) dissolved in 5 mL ethanol:water (1:1) was slowly added to a solution of sodium ascorbate (70 mg, 0.35 mmol) in 5 mL ethanol:water (1:1). A separate vessel was charged with **12** (50 mg, 0.087 mmol) and ferrocenyl methyl azide (45.3 mg, 0.19 mmol) to which the copper solution was slowly added and the reaction mixture was allowed to stir for 1 hour. Dichloromethane (10 mL) was added and the reaction mixture was rapidly stirred overnight. Once complete, as monitored via TLC, the reaction was quenched by the addition of cold water (50 mL), and the product was extracted with dichloromethane (3× 25 mL), and dried using MgSO₄. The filtrate was concentrated *in vacuo*, and the residue was purified using flash chromatography (acetone/petroleum ether 1:3) to afford **11** as a yellow solid (85 mg, 64%). ¹H NMR (500 MHz, CDCl₃): 2.86 (d, *J* = 13.0 Hz, 4H), 4.09 (d, *J* = 13.0 Hz, 4H), 4.28 – 4.14 (m, 36H), 4.96 (s, 8H), 5.19 (s, 8H), 6.51 (s, 12H), 7.66 (s, 4H). ¹³C NMR (125 MHz, CDCl₃): 31.27, 49.90, 66.50, 68.78, 68.87, 68.93, 81.86, 122.56, 123.90, 128.11, 135.30, 144.19, 154.63; IR (neat, ν / cm⁻¹): 3085, 2919, 2243, 1709, 1584, 1457, 1432, 1195; HRMS: *m/z*: [M + 2H]²⁺ Calcd for C₈₄H₇₈N₁₂O₄Fe₄, 771.1834, found 771.1831.

Spectroscopic data for compounds 1-13

Compound 1

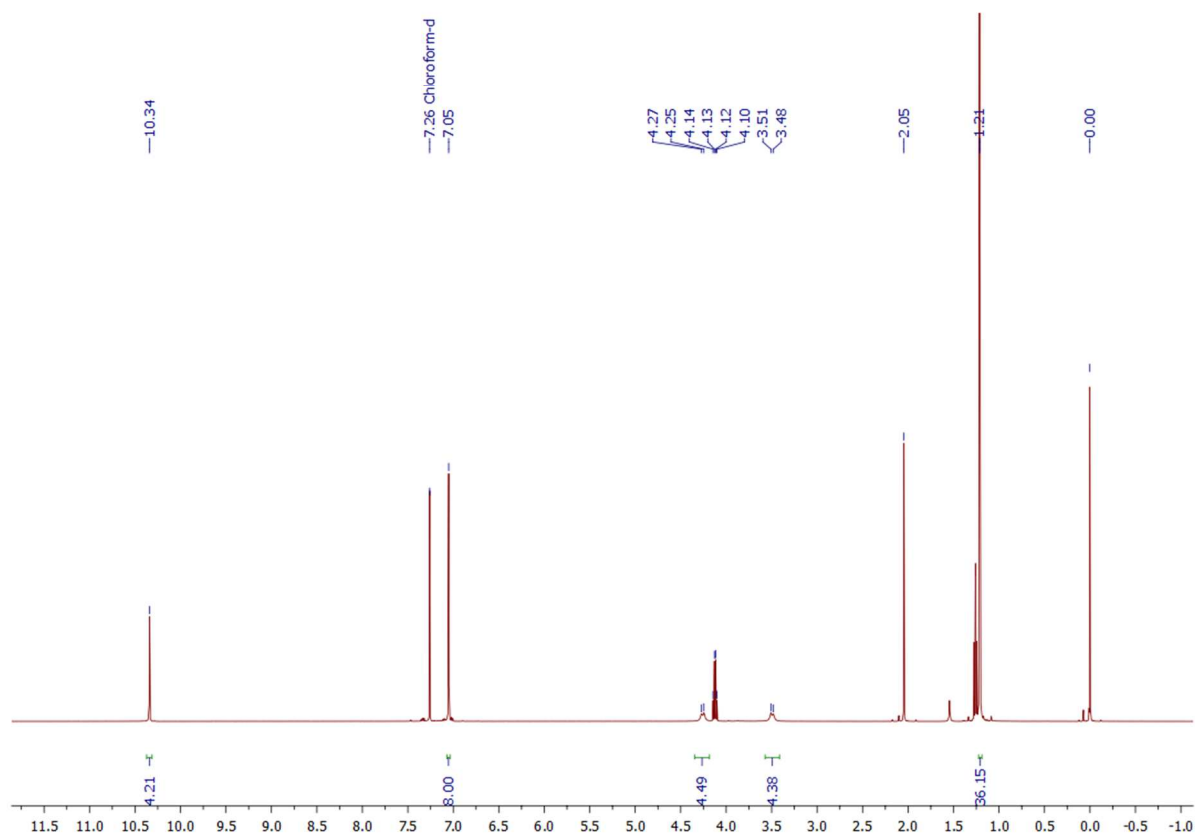


Figure S-1. ¹H NMR spectrum of compound 1 in CDCl₃.

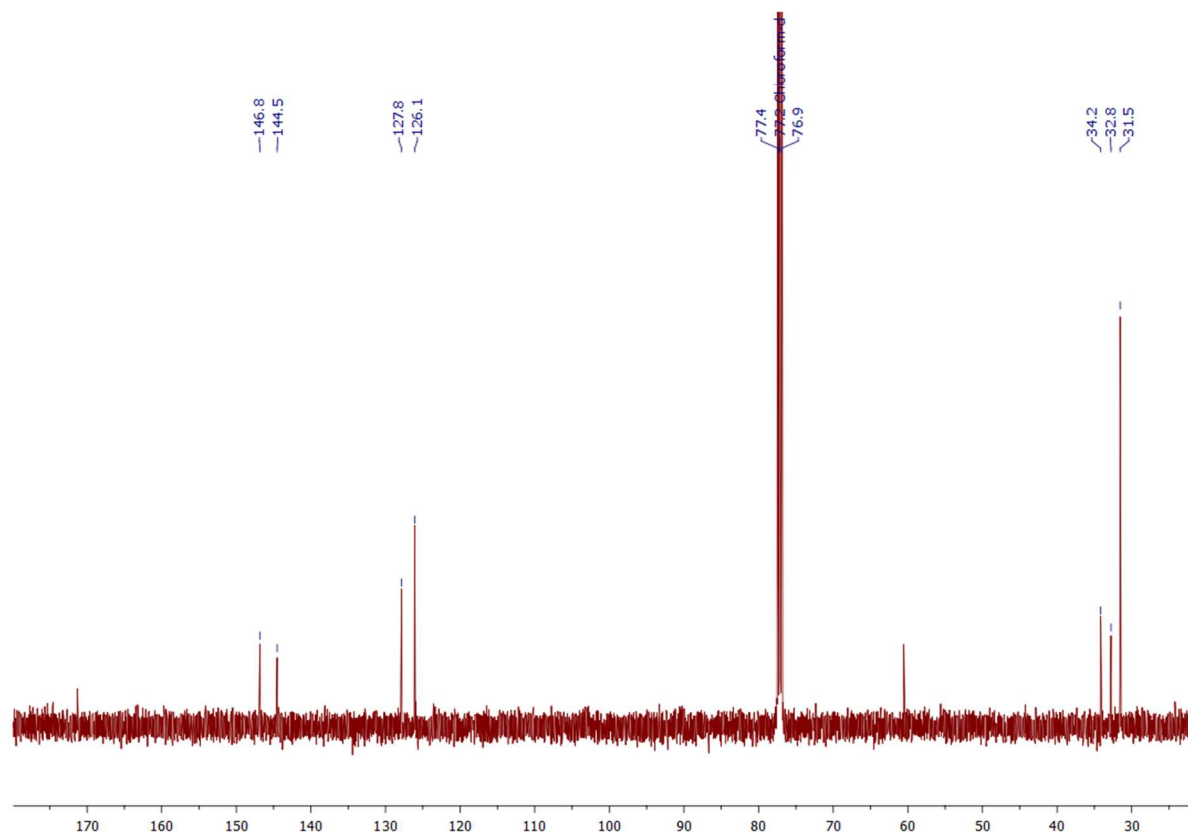


Figure S-2. ^{13}C NMR spectrum of compound **1** in CDCl_3 .

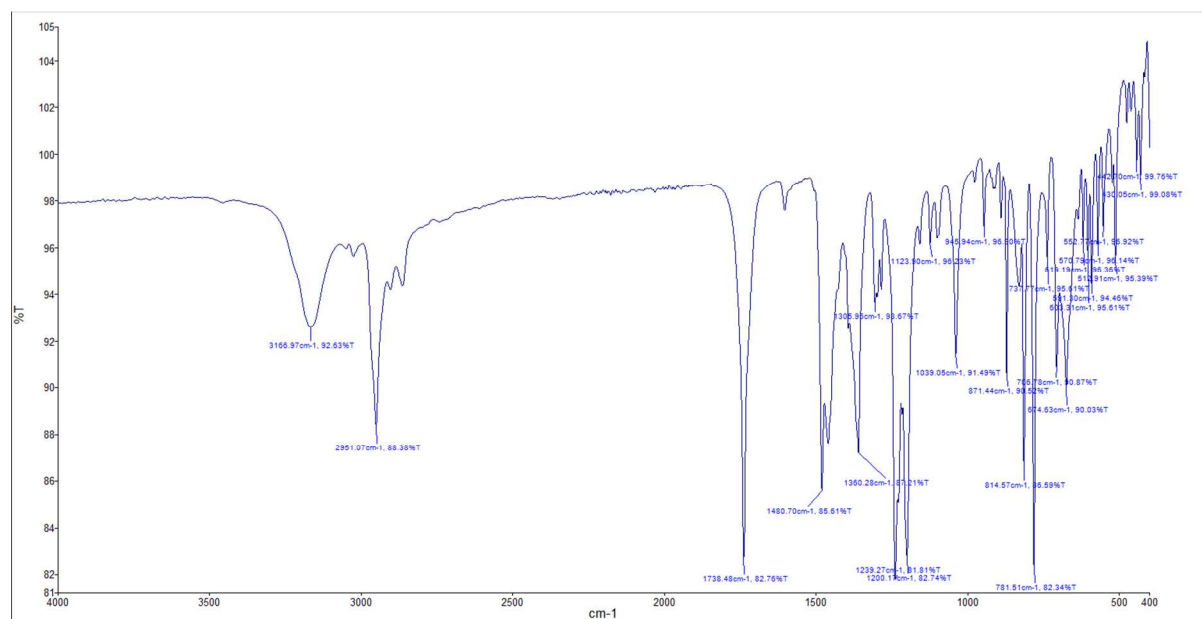


Figure S-3. IR spectrum of compound **1**.

Compound 2

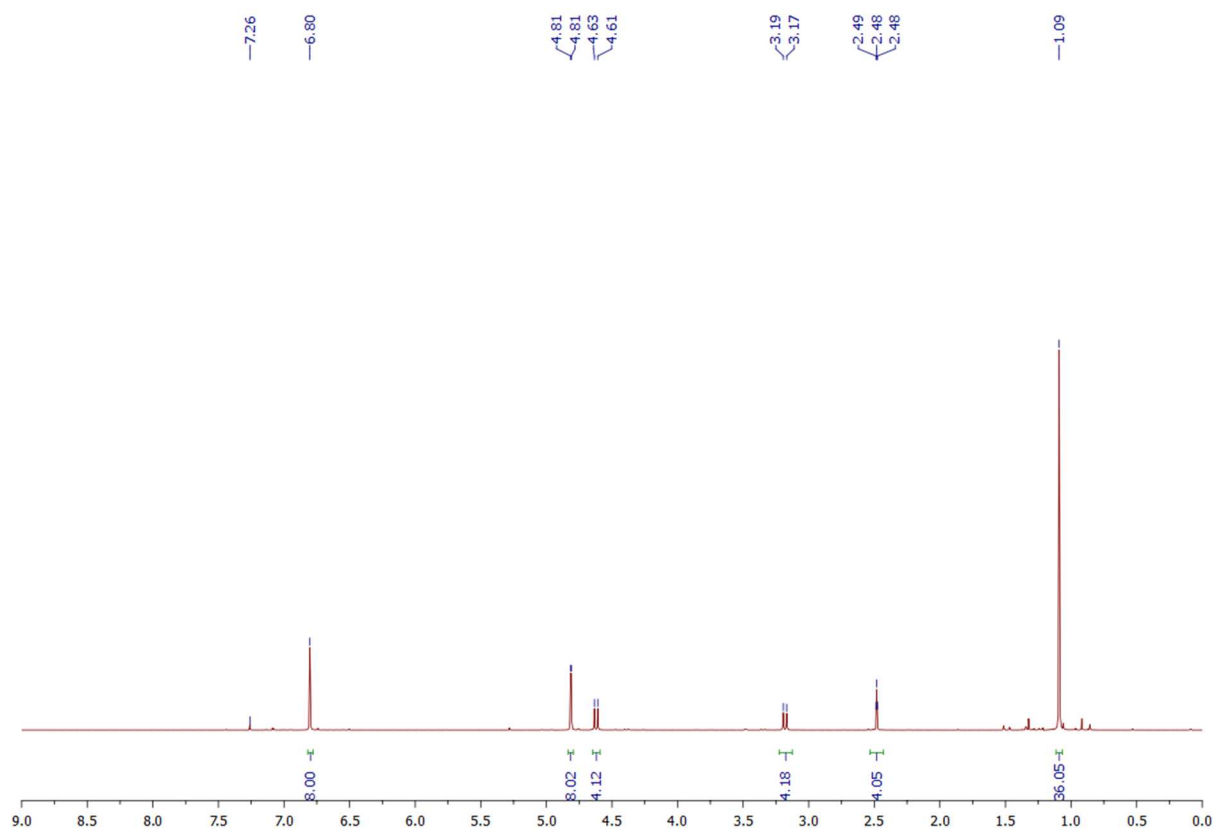


Figure S-4. ¹H NMR spectrum of compound **2** in CDCl₃.

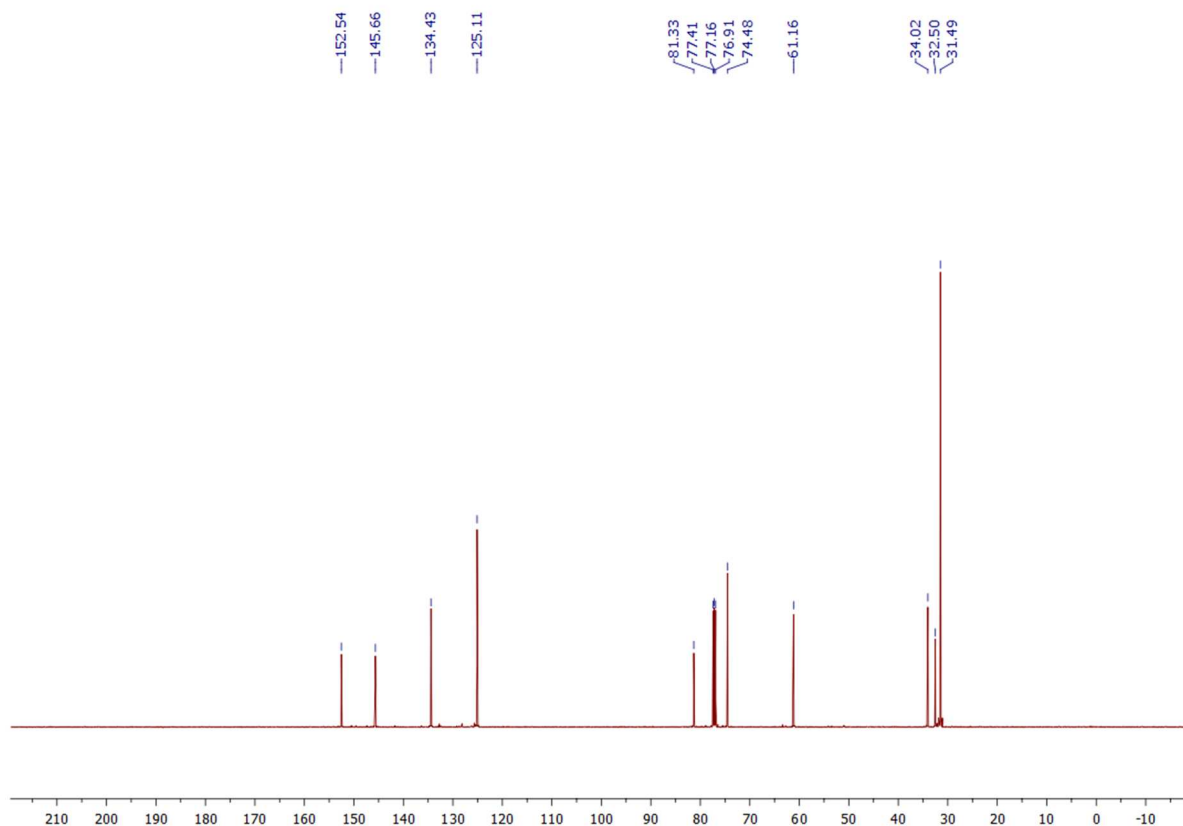


Figure S-5. ^{13}C NMR spectrum of compound **2** in CDCl_3 .

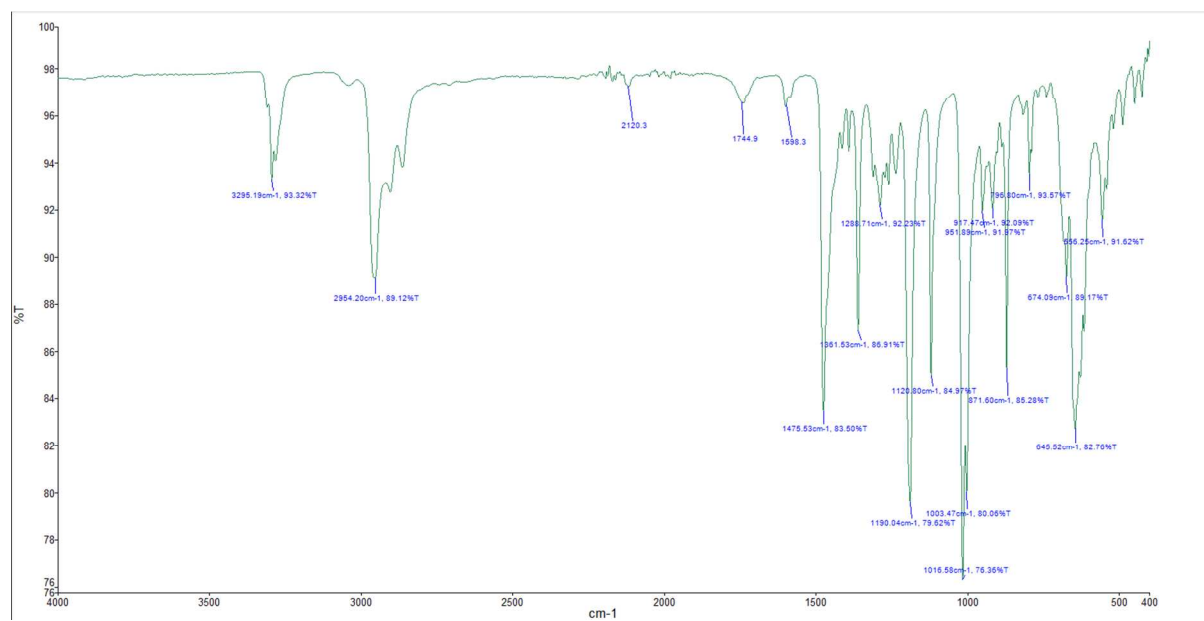


Figure S-6. IR spectrum of compound **2**.

Compound 3

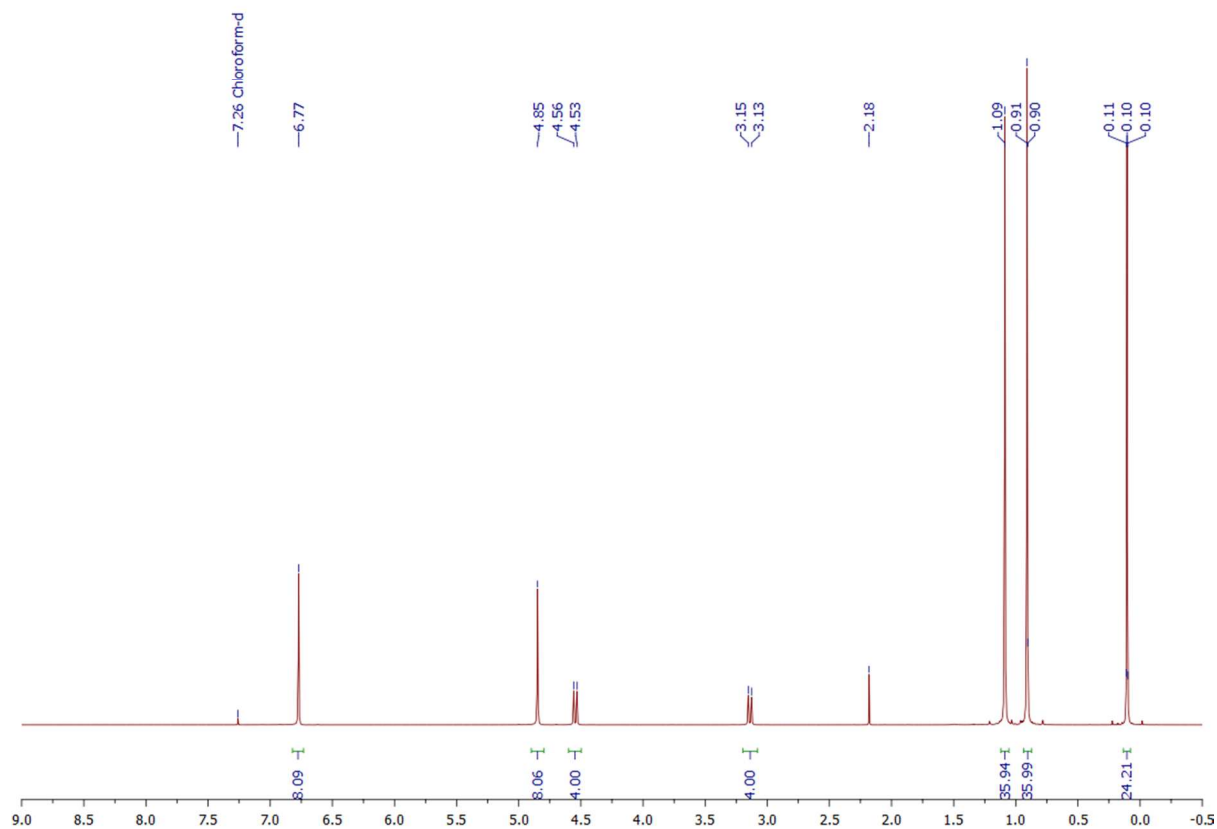


Figure S-7. ¹H NMR spectrum of compound **3** in CDCl₃.

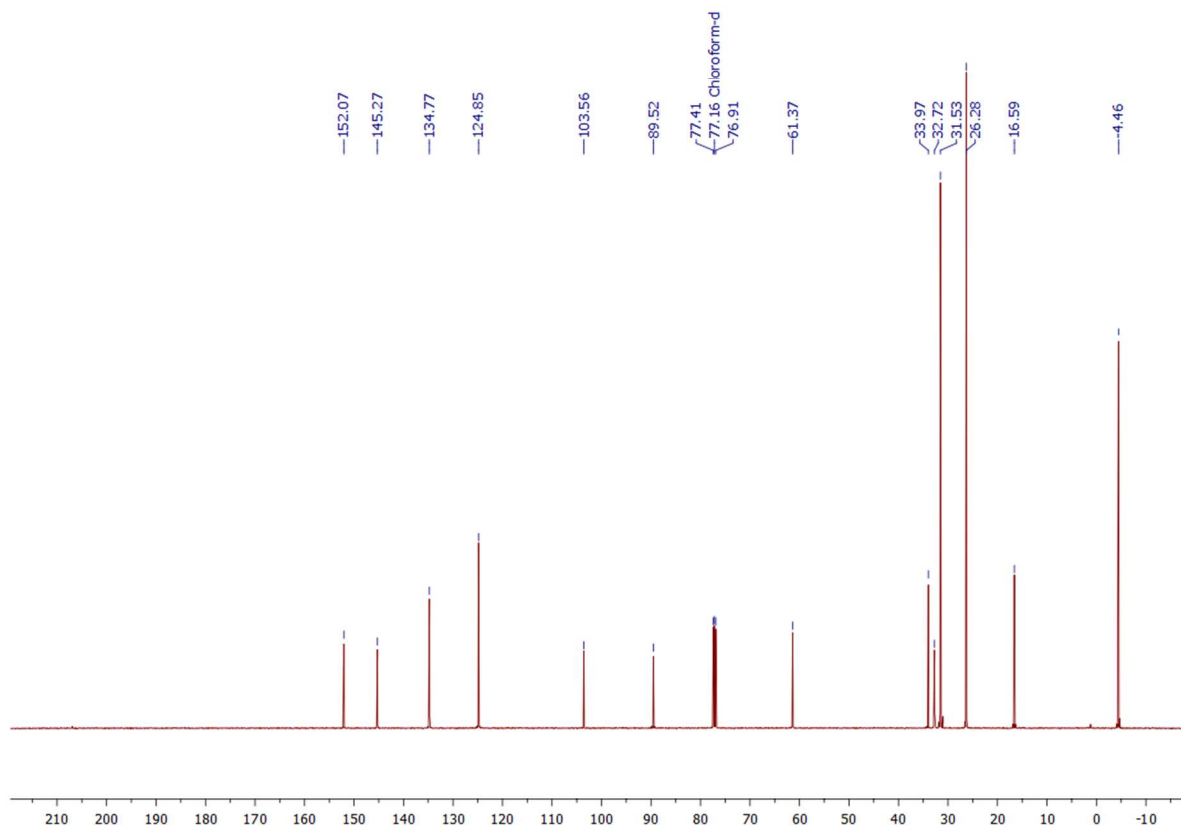


Figure S-8. ^{13}C NMR spectrum of compound **3** in CDCl_3 .

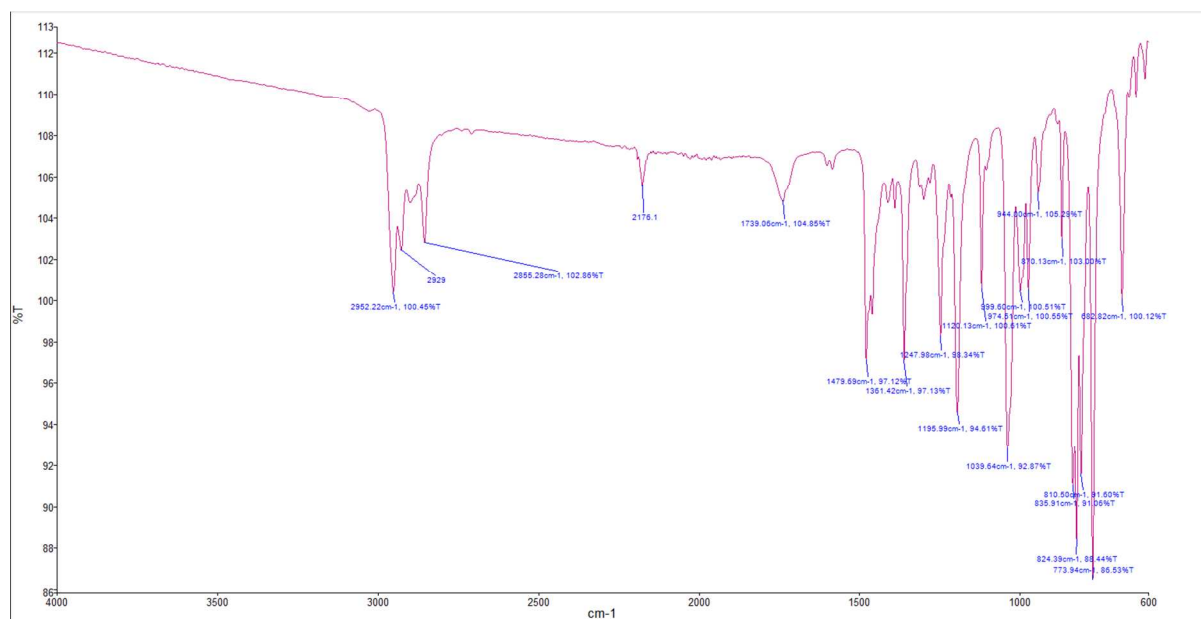


Figure S-9. IR spectrum of compound **3**.

Compound 4

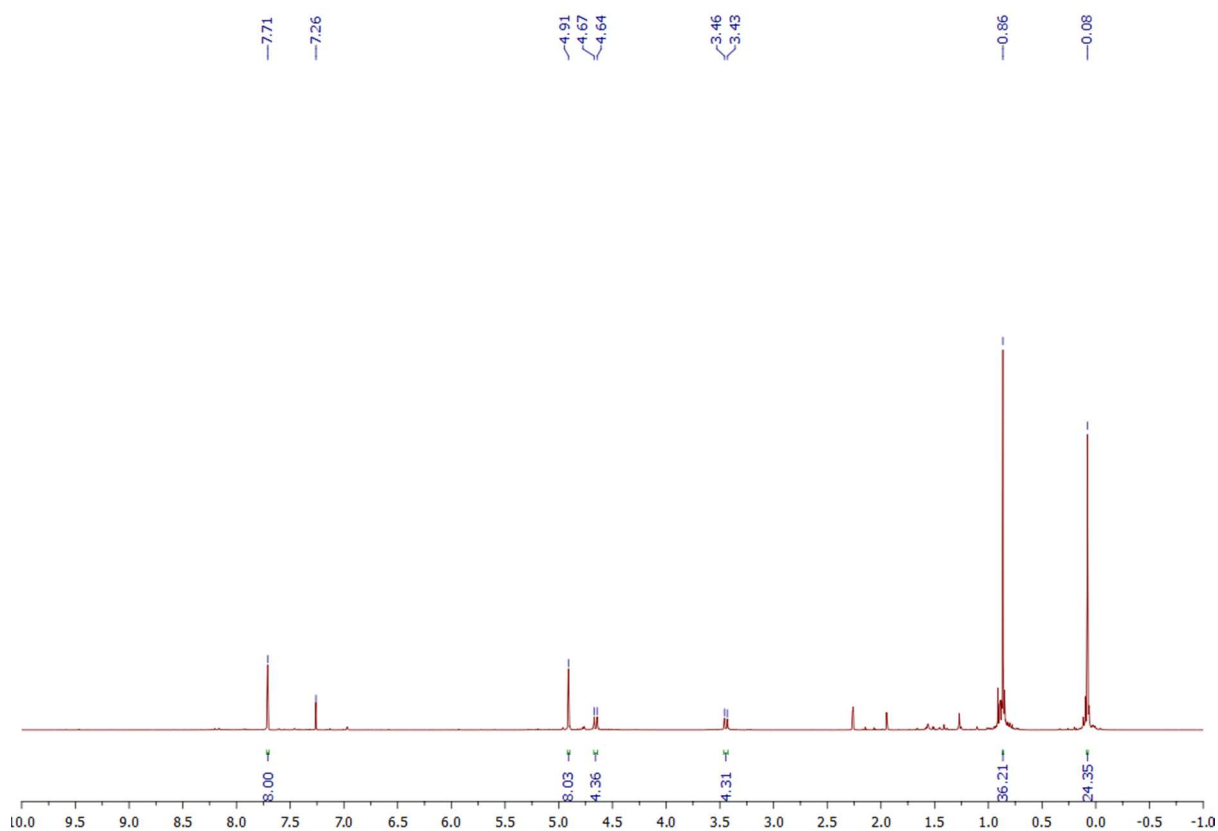


Figure S-10. ¹H NMR spectrum of compound **4** in CDCl₃.

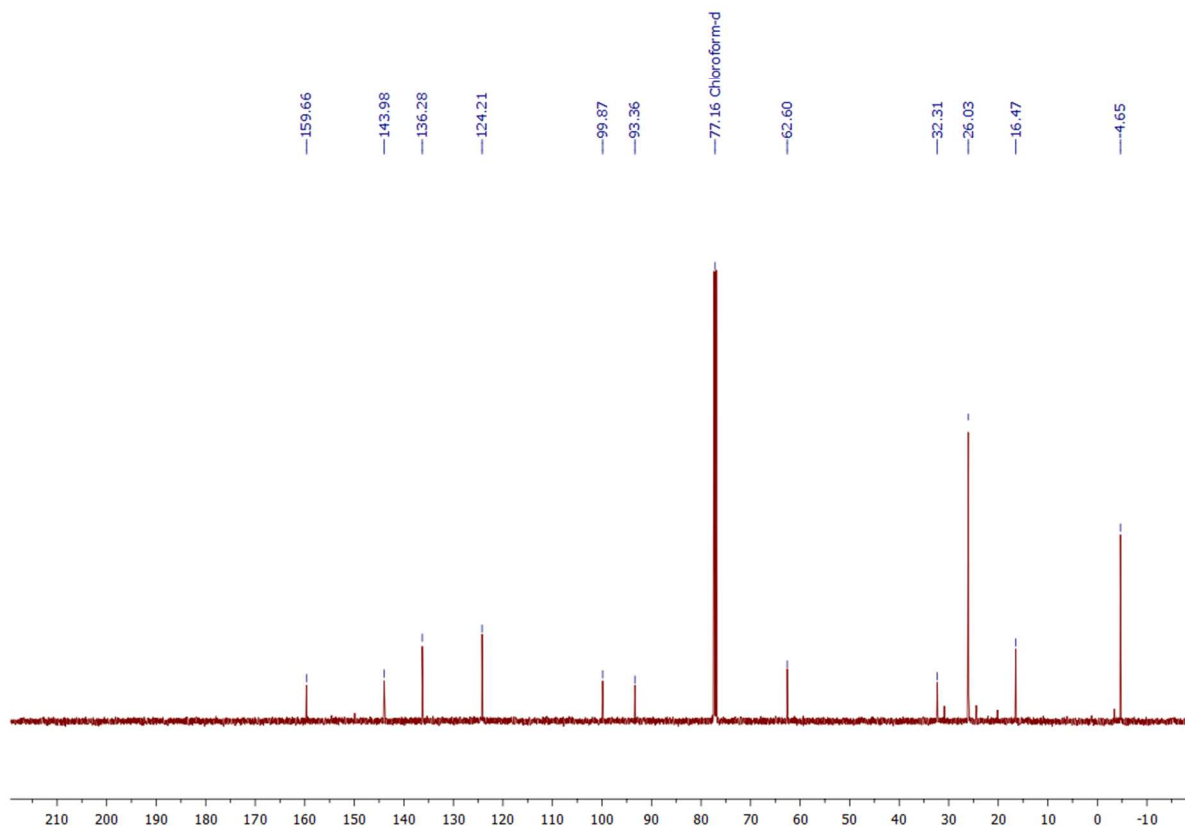


Figure S-11. ^{13}C NMR spectrum of compound **4** in CDCl_3 .

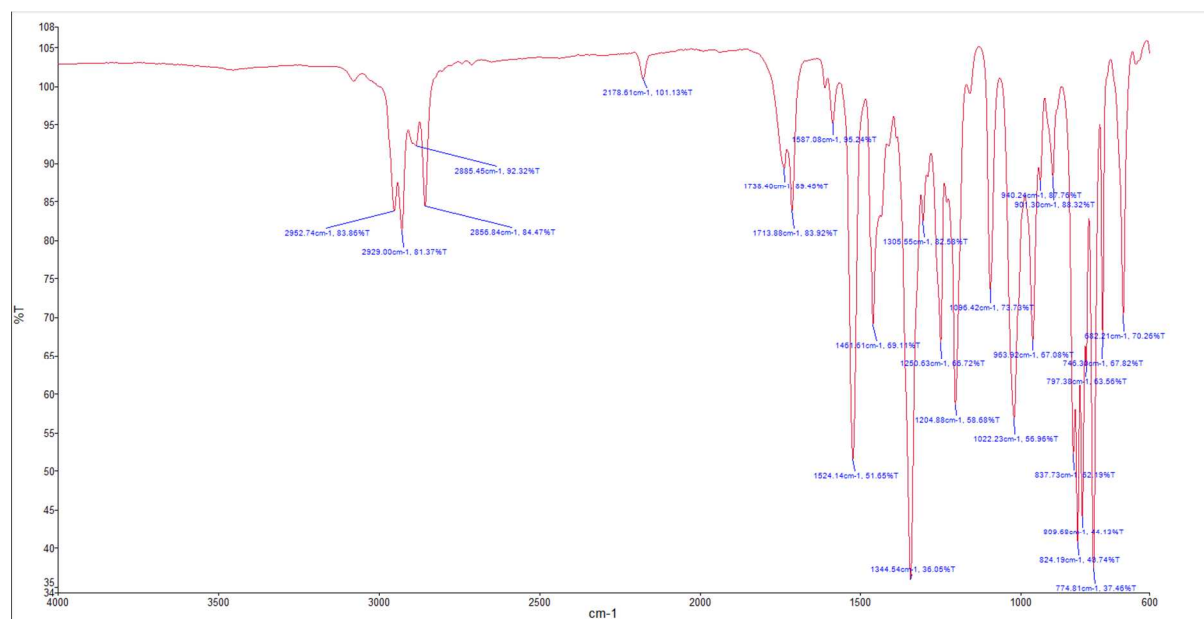


Figure S-12. IR spectrum of compound **4**.

Compound 5

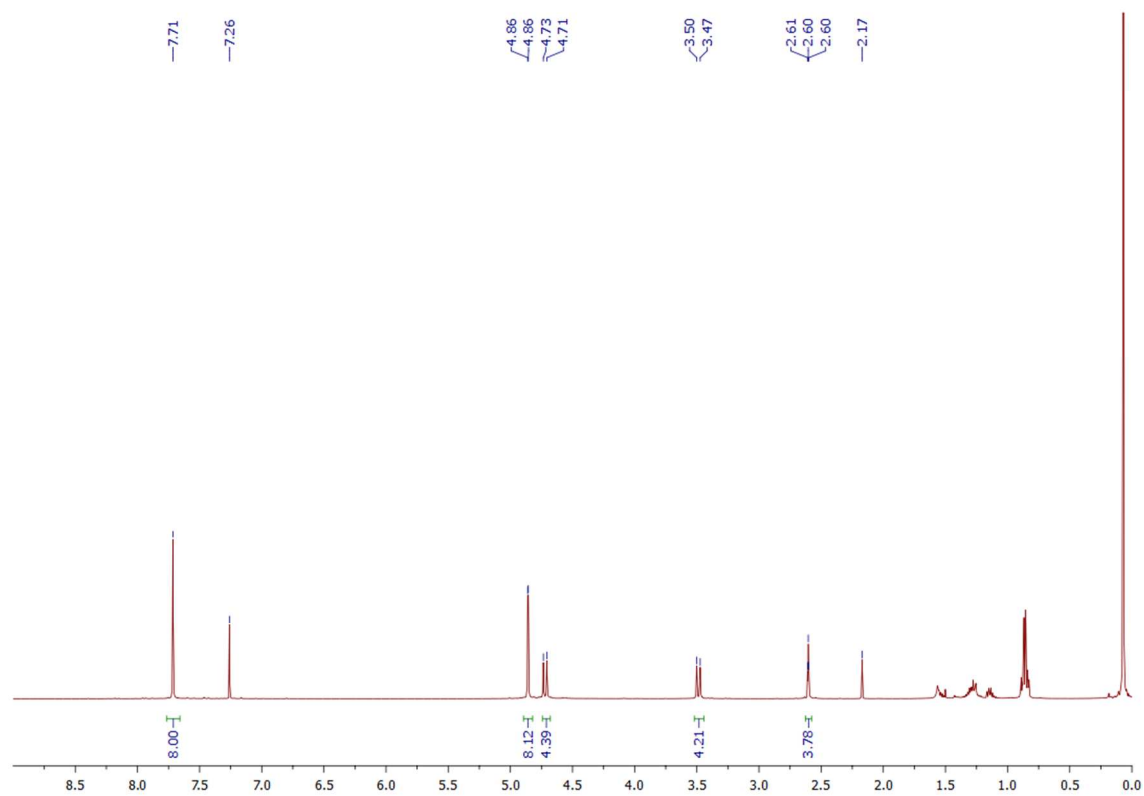


Figure S-13. ¹H NMR spectrum of compound 5 in CDCl₃.

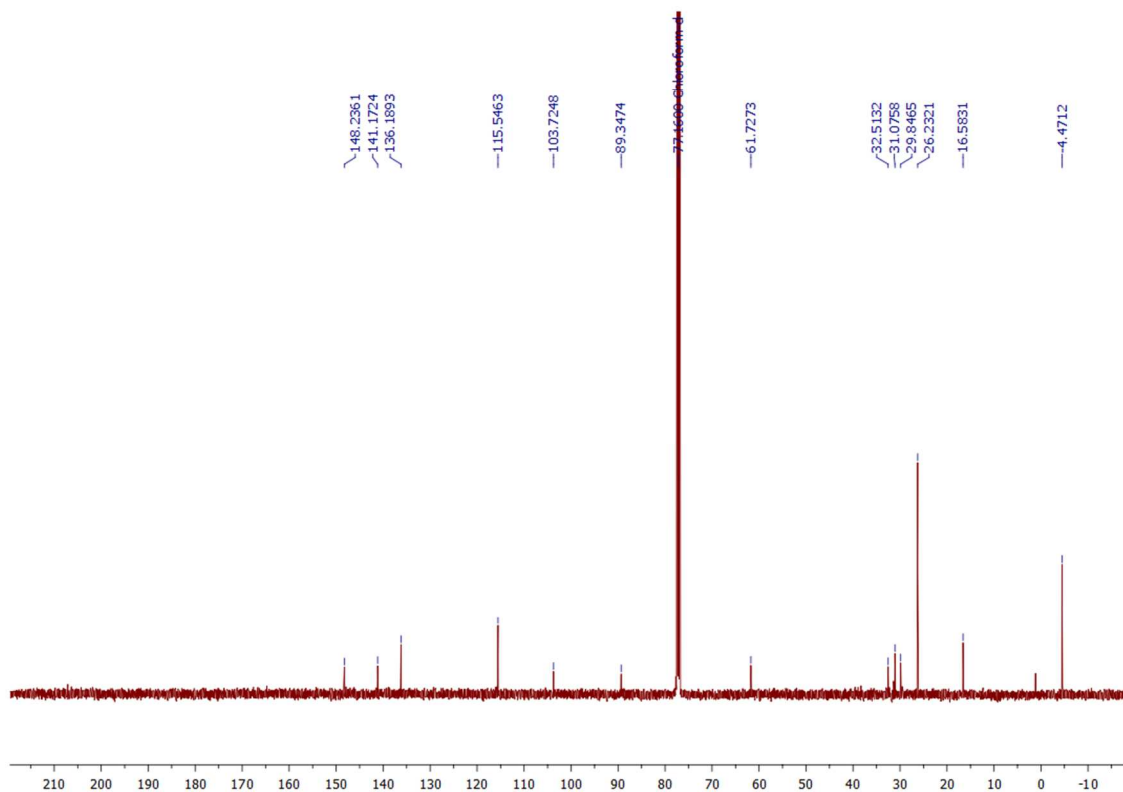


Figure S-14. ¹³C NMR spectrum of compound 5 in CDCl₃.

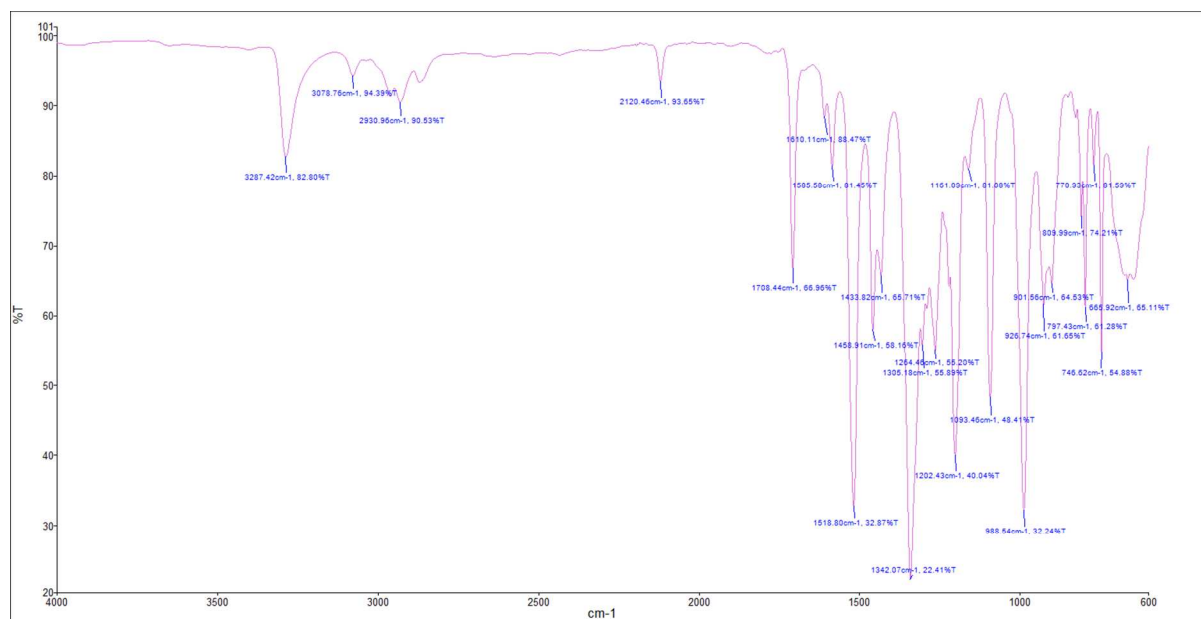


Figure S-15. IR spectrum of compound 5.

Compound 6

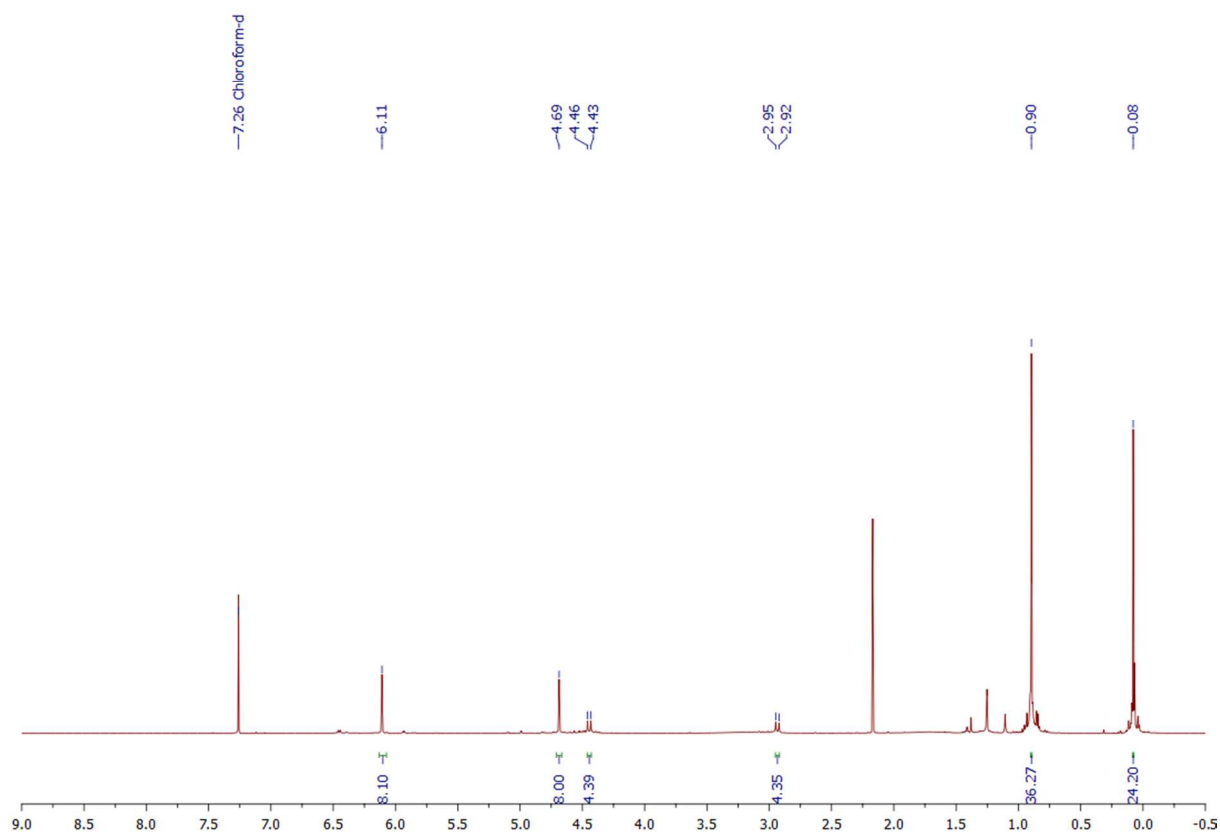


Figure S-16. ¹H NMR spectrum of compound 6 in CDCl₃.

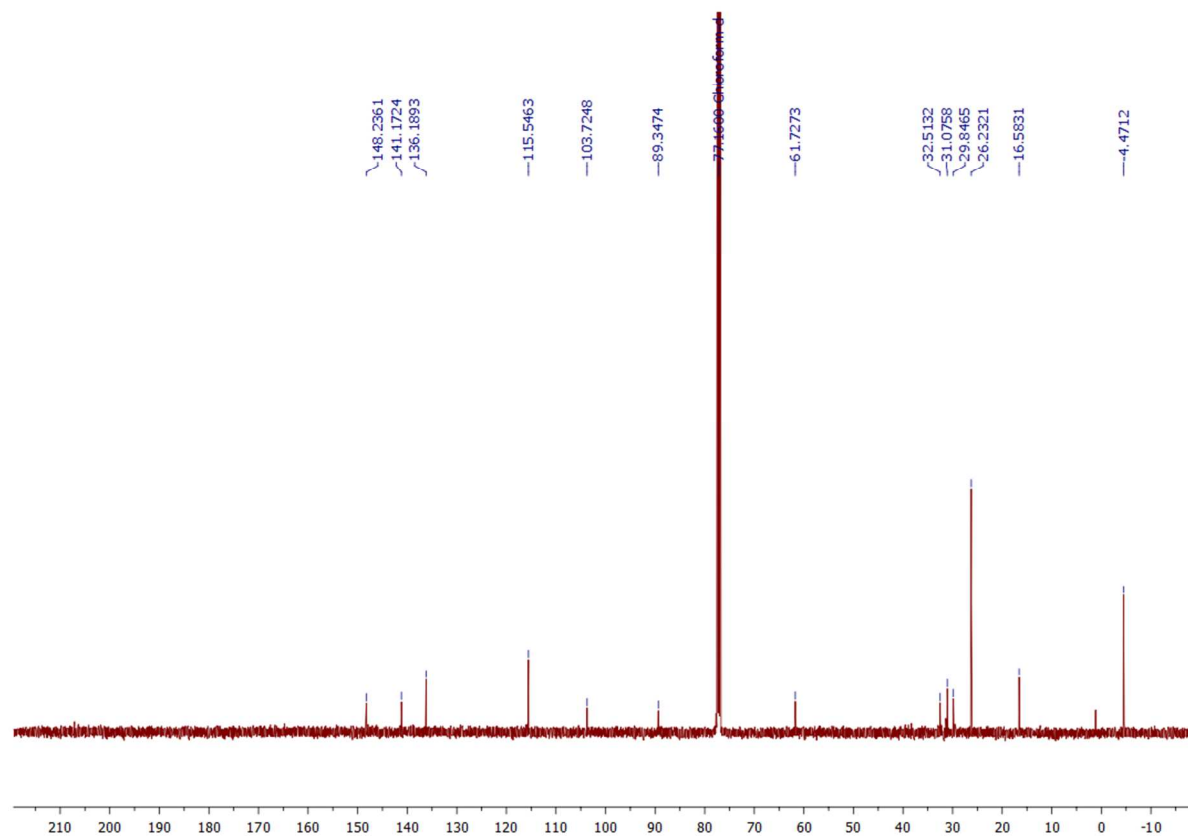


Figure S-17. ¹³C NMR spectrum of compound 6 in CDCl₃.

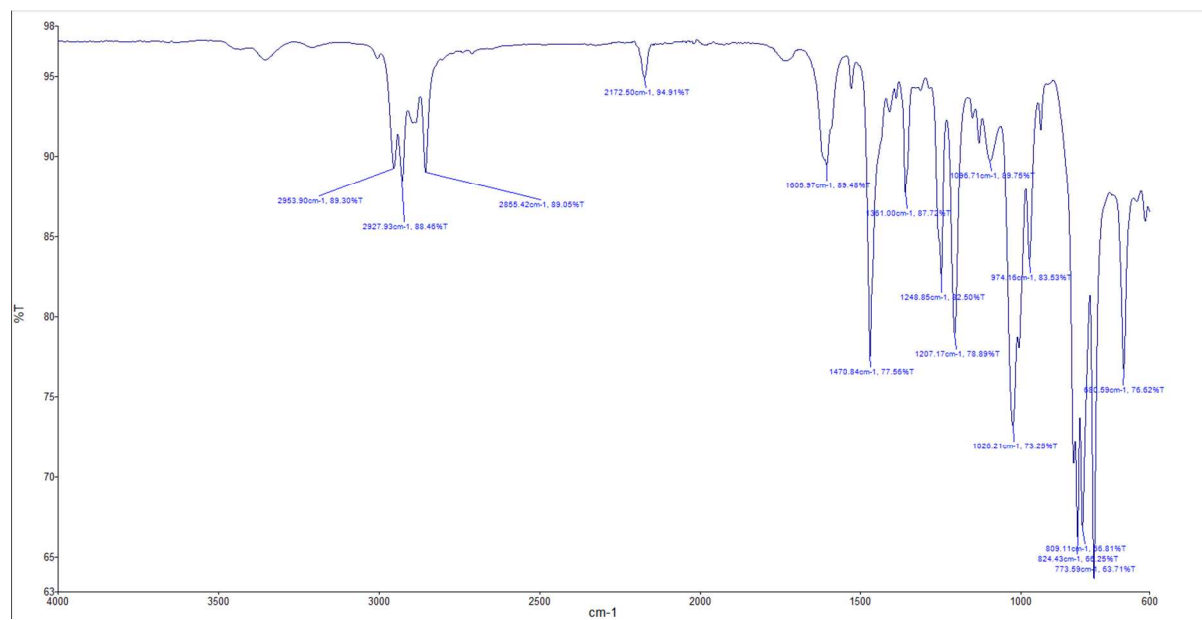


Figure S-18. IR spectrum of compound 6.

Compound 7

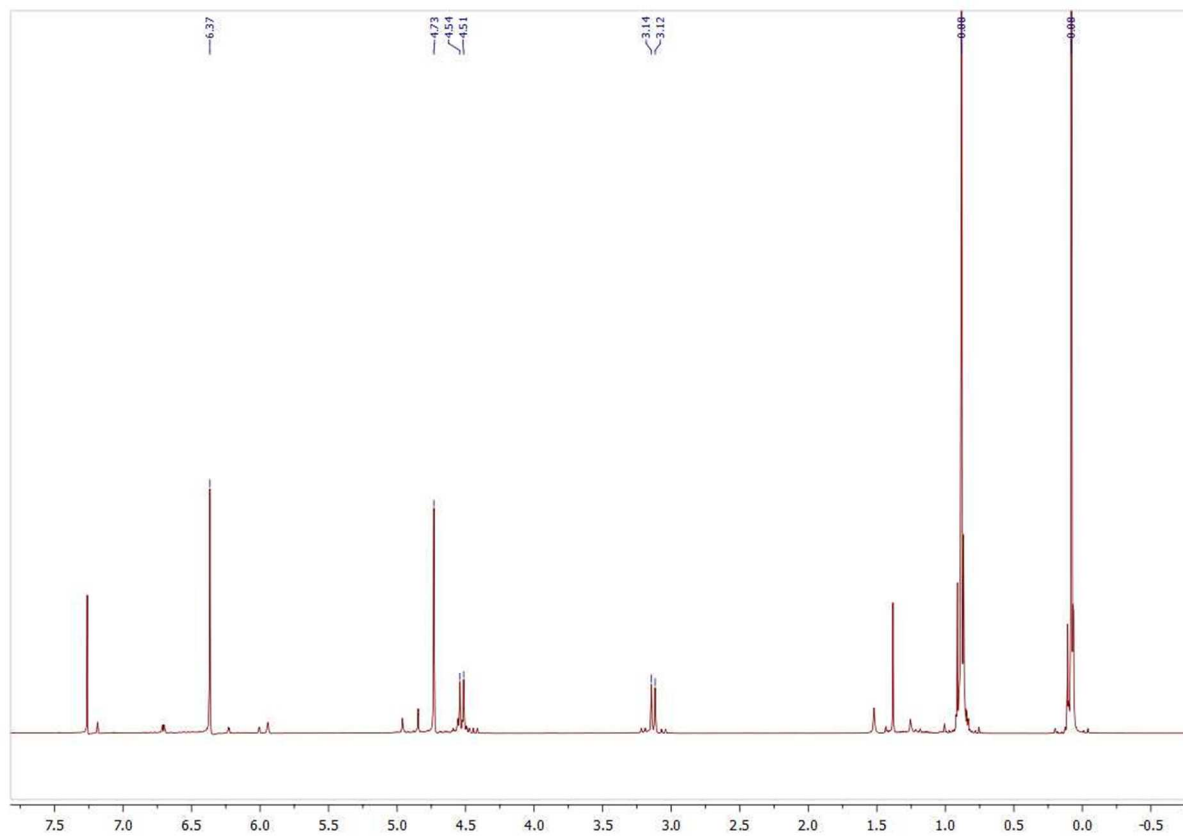


Figure S-19. ^1H NMR spectrum of compound **7** in CDCl_3 .

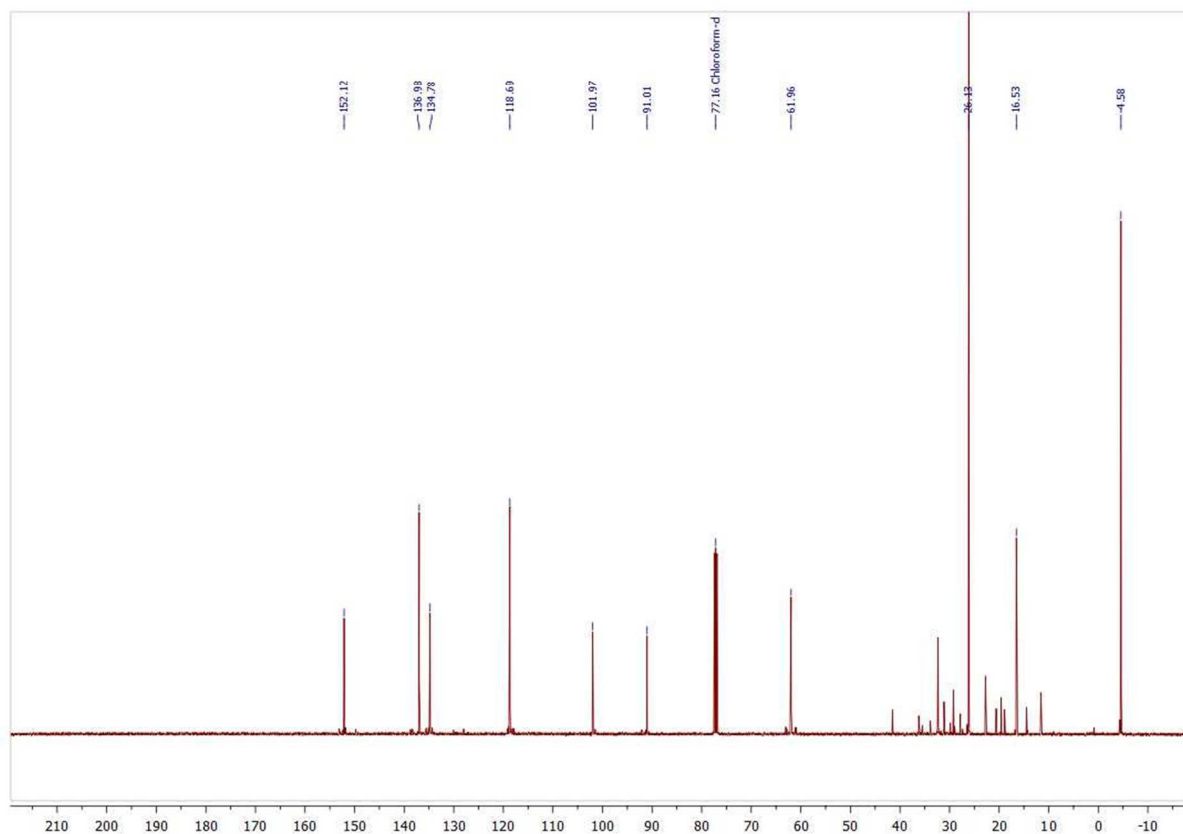


Figure S-20. ¹³C NMR spectrum of compound **7** in CDCl₃.

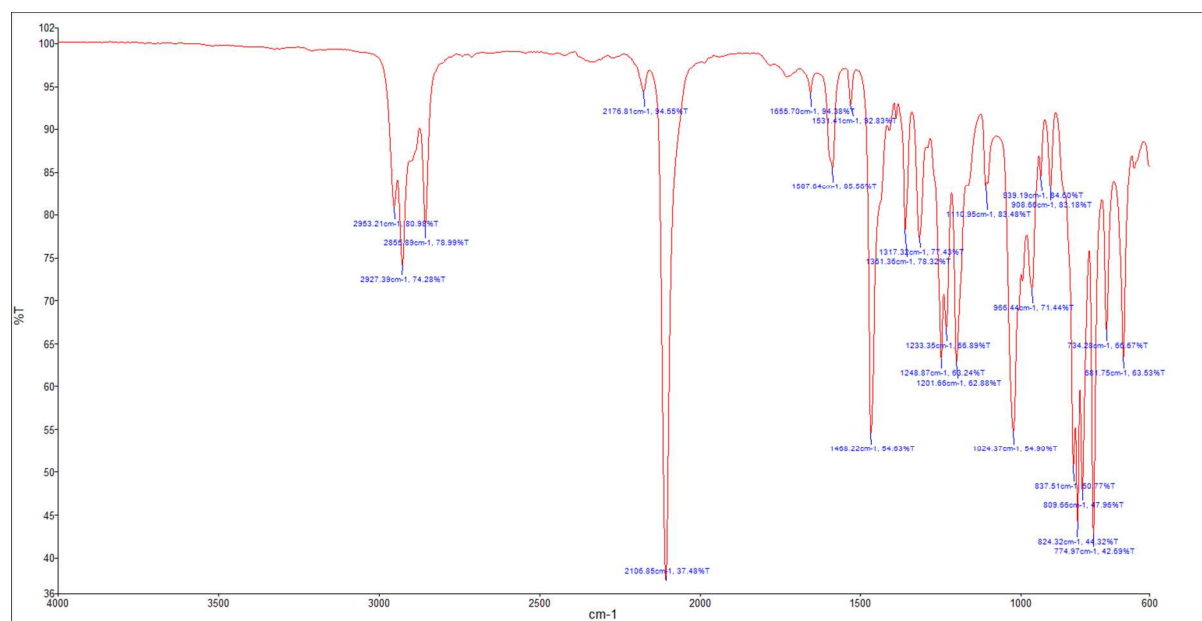


Figure S-21. IR spectrum of compound **7**.

Compound 8

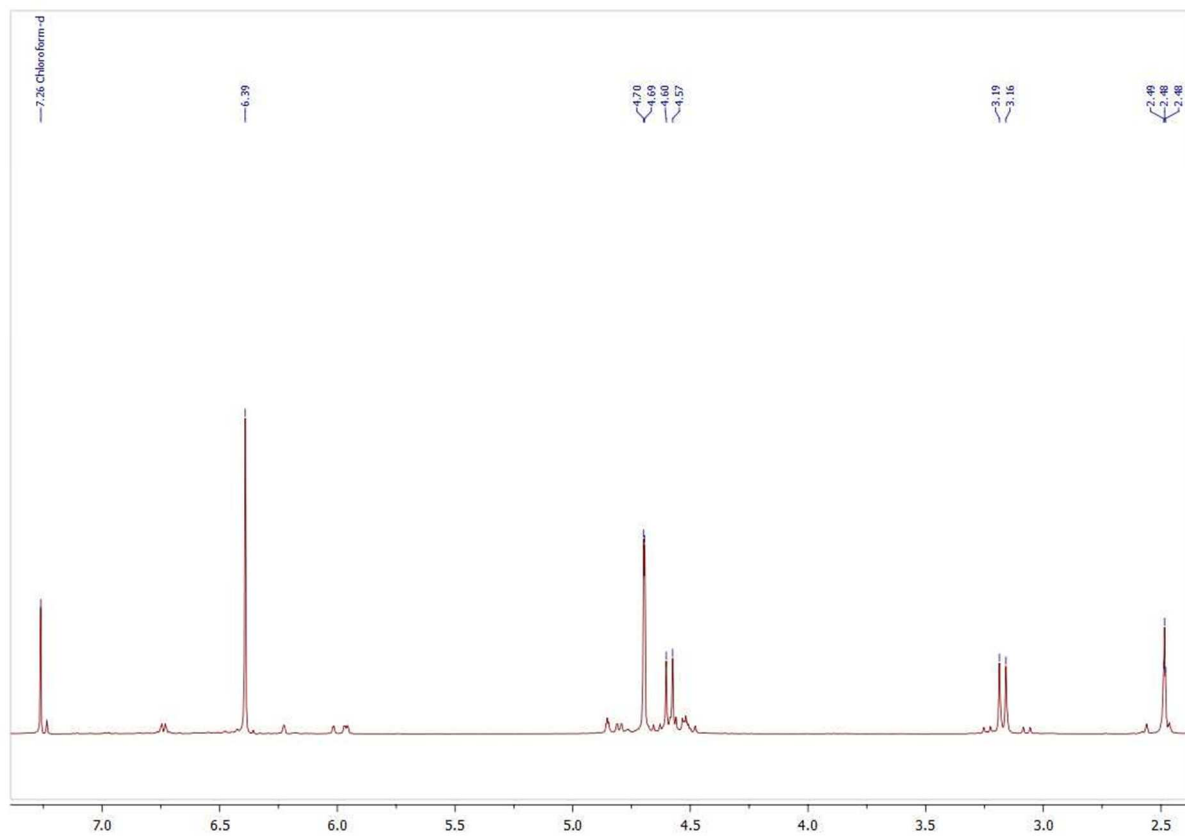


Figure S-22. ^1H NMR spectrum of compound **8** in CDCl_3 .

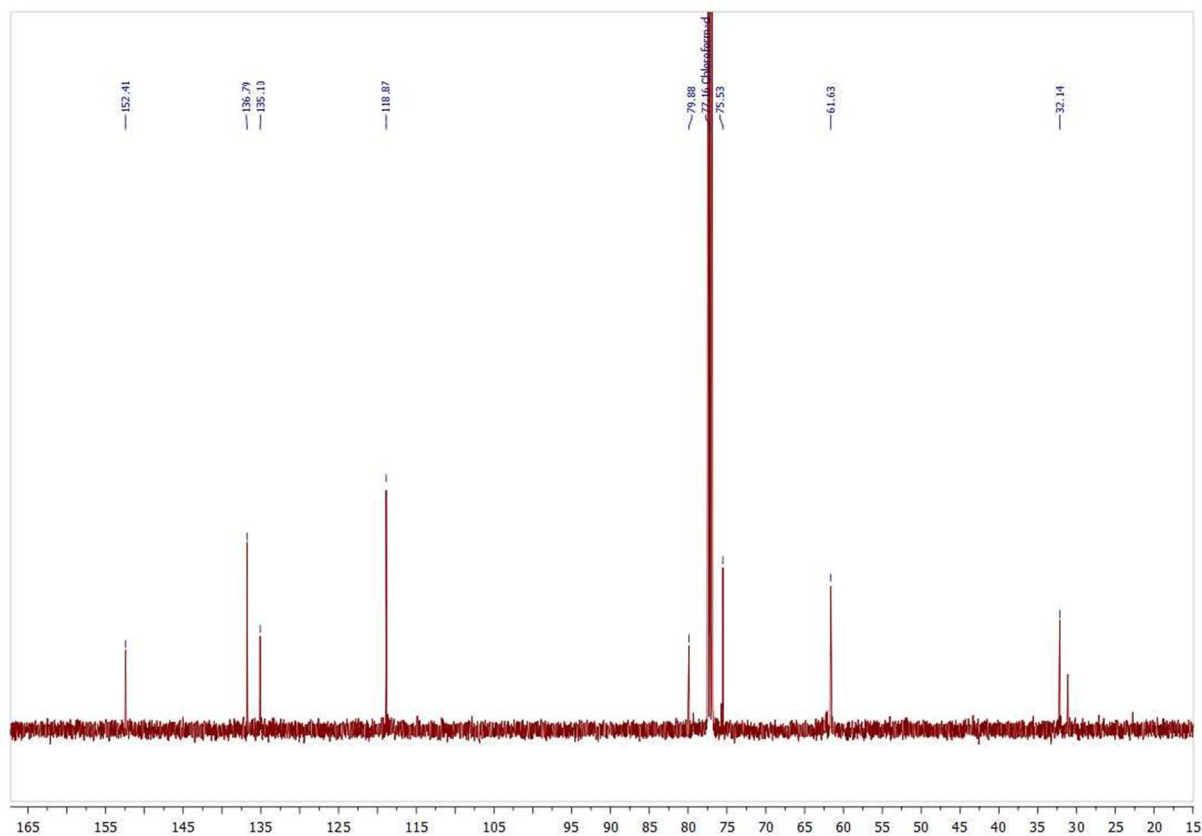


Figure S-23. ^{13}C NMR spectrum of compound **8** in CDCl_3 .

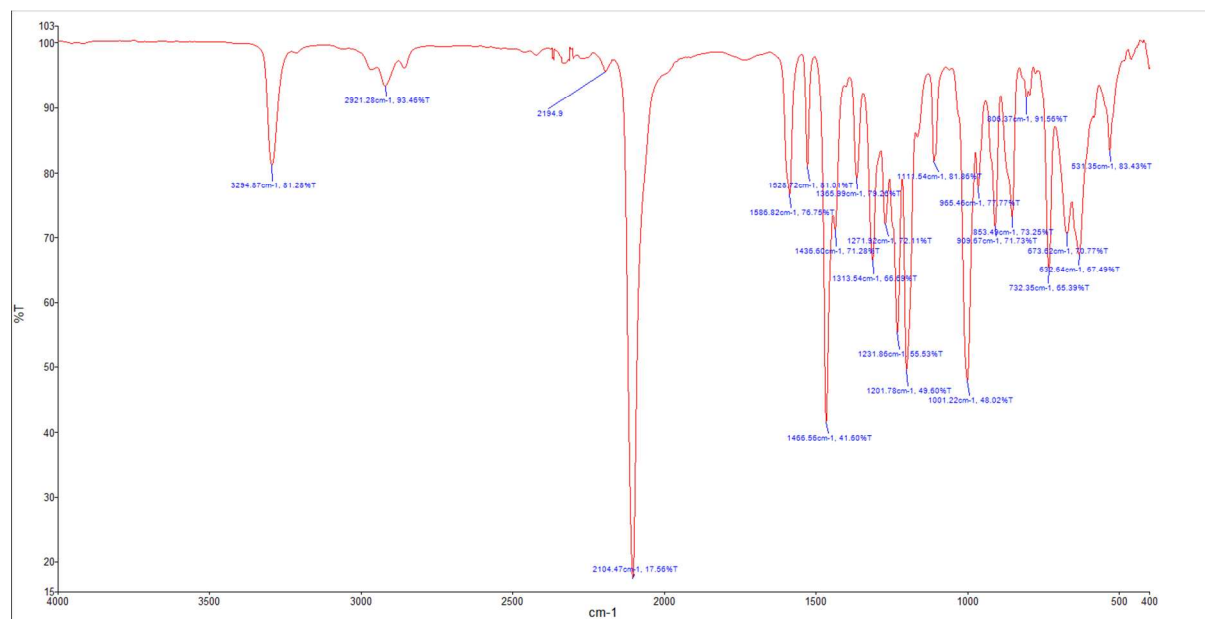


Figure S-24. IR spectrum of compound **8**.

Compound 9

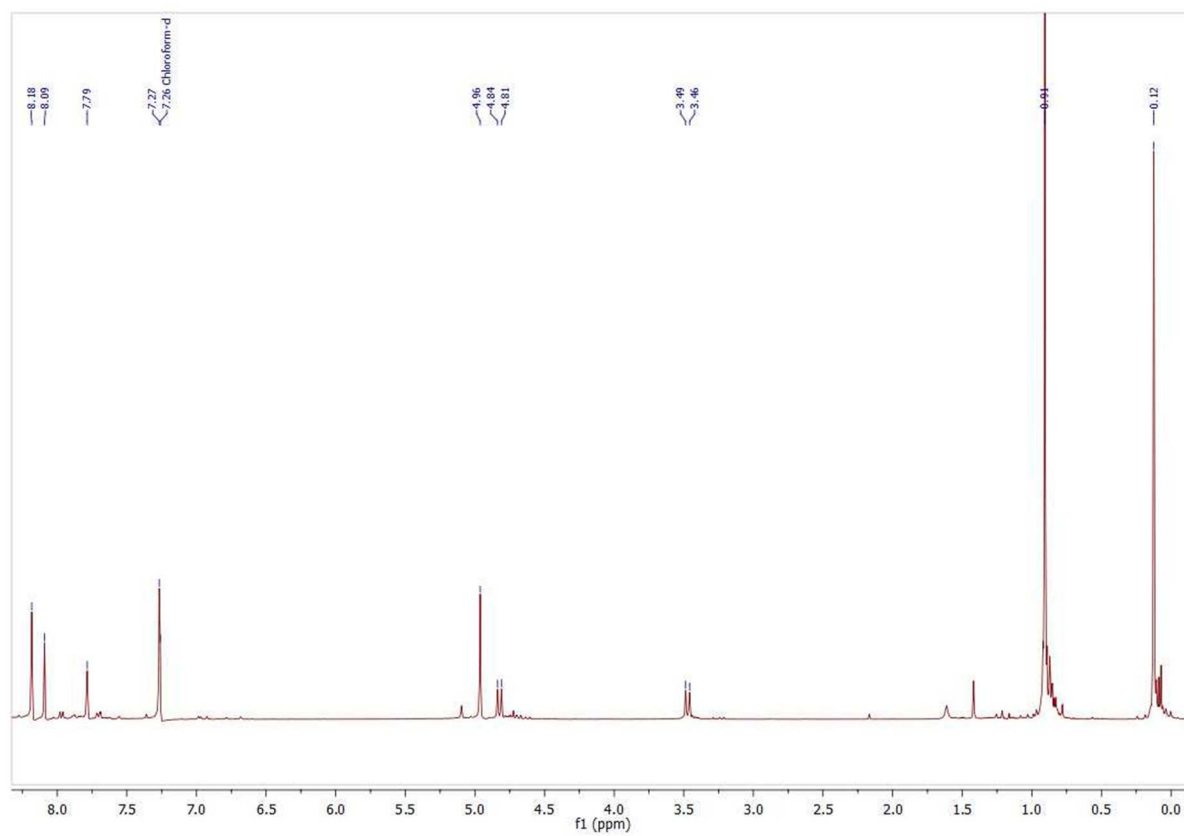


Figure S-25. ^1H NMR spectrum of compound 9 in CDCl_3 .

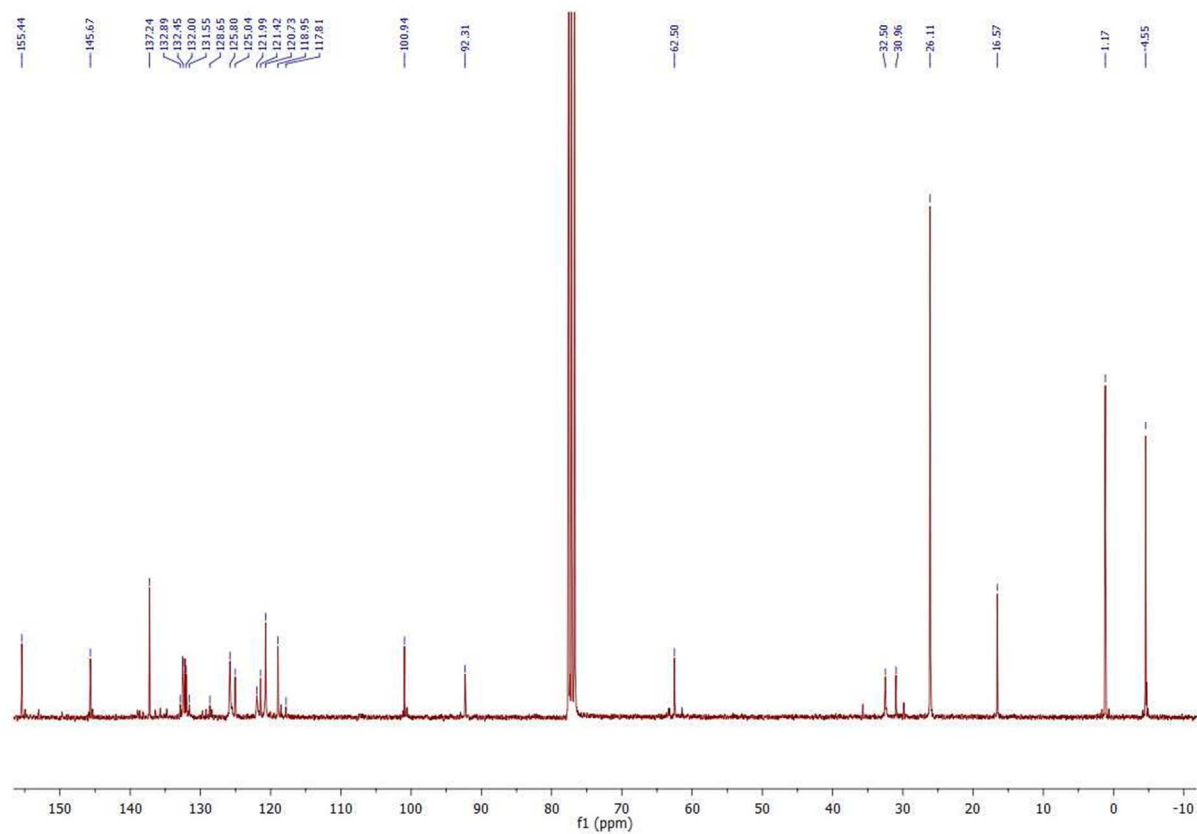


Figure S-26. ¹³C NMR spectrum of compound 9 in CDCl₃.

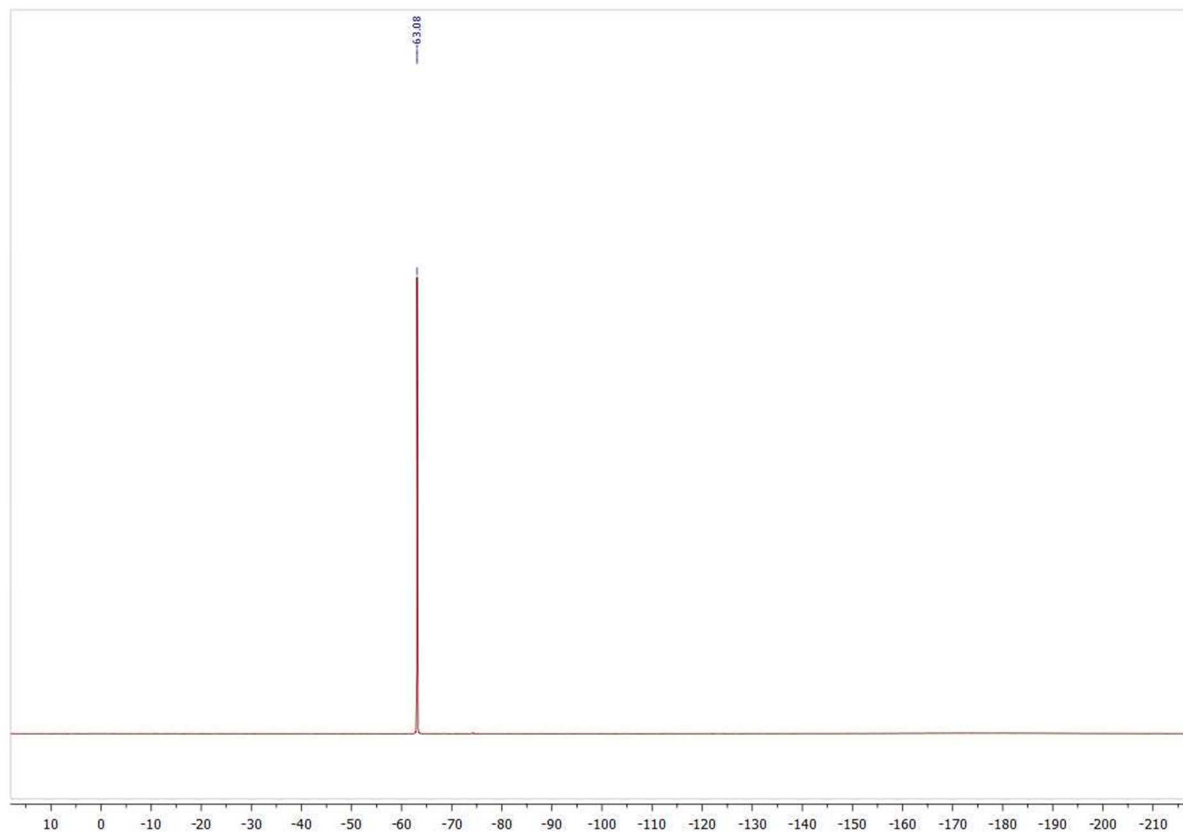


Figure S-27. ^{19}F NMR spectrum of compound 9.

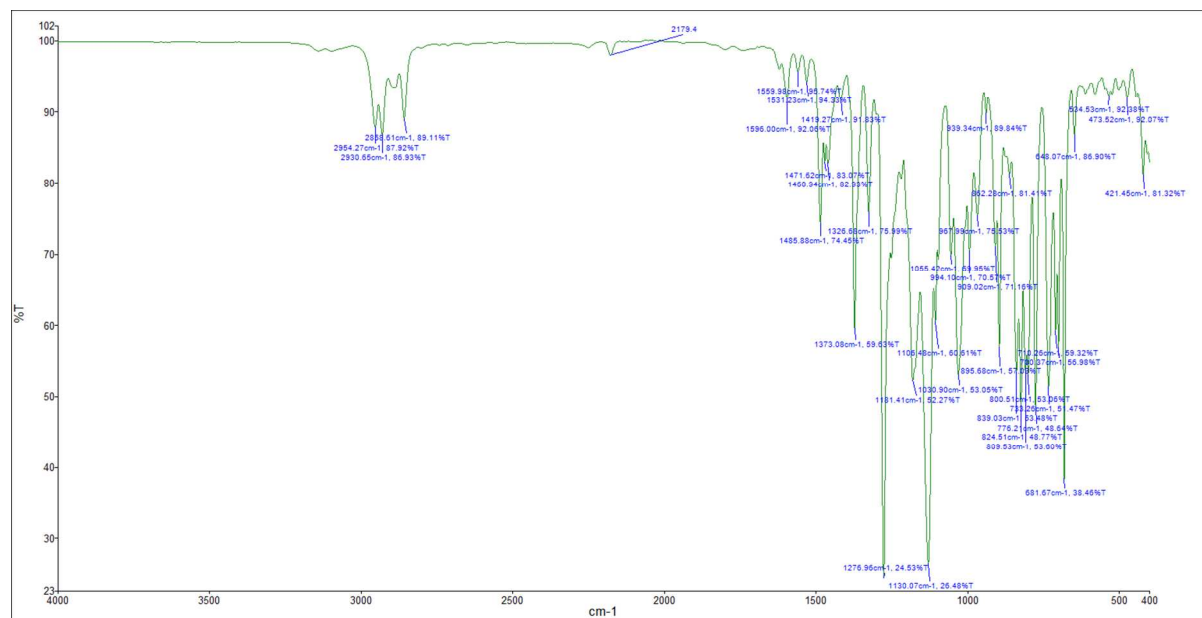


Figure S-28. IR spectrum of compound 9.

Compound 10

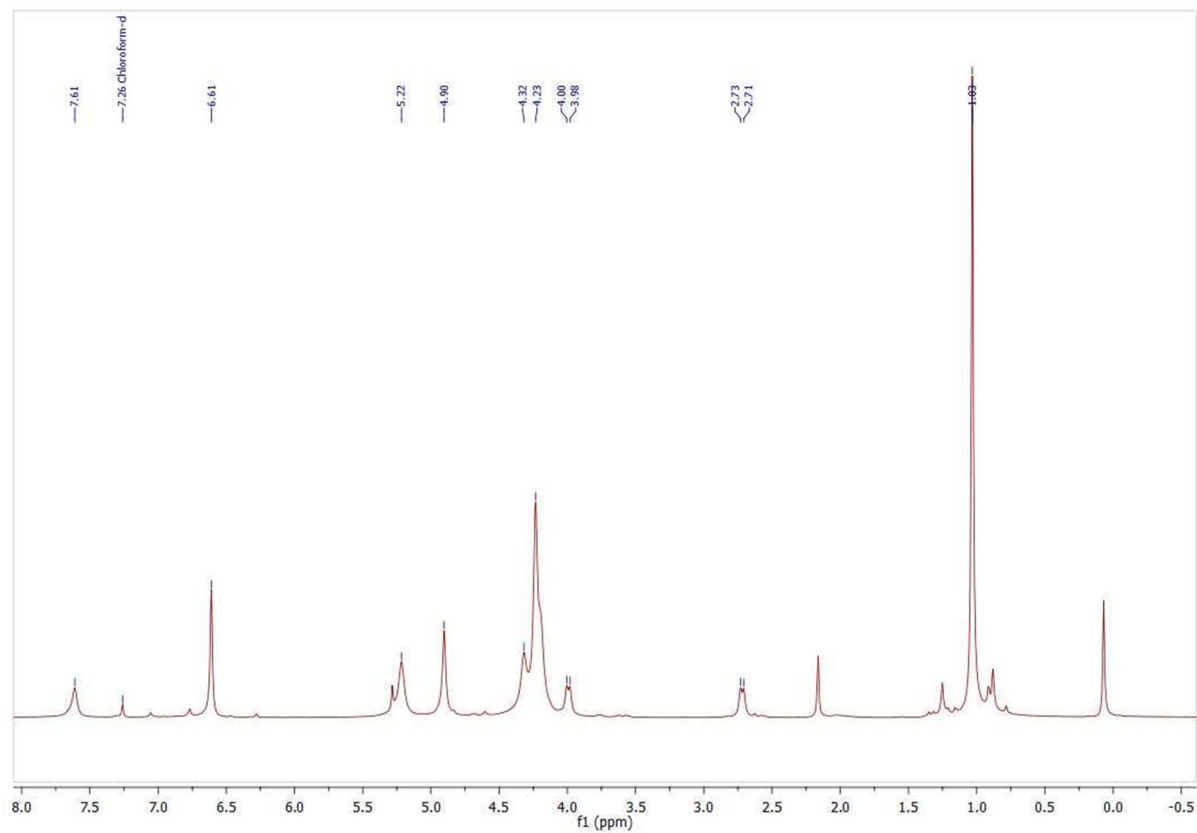


Figure S-29. ^1H NMR spectrum of compound **10** in CDCl_3 .

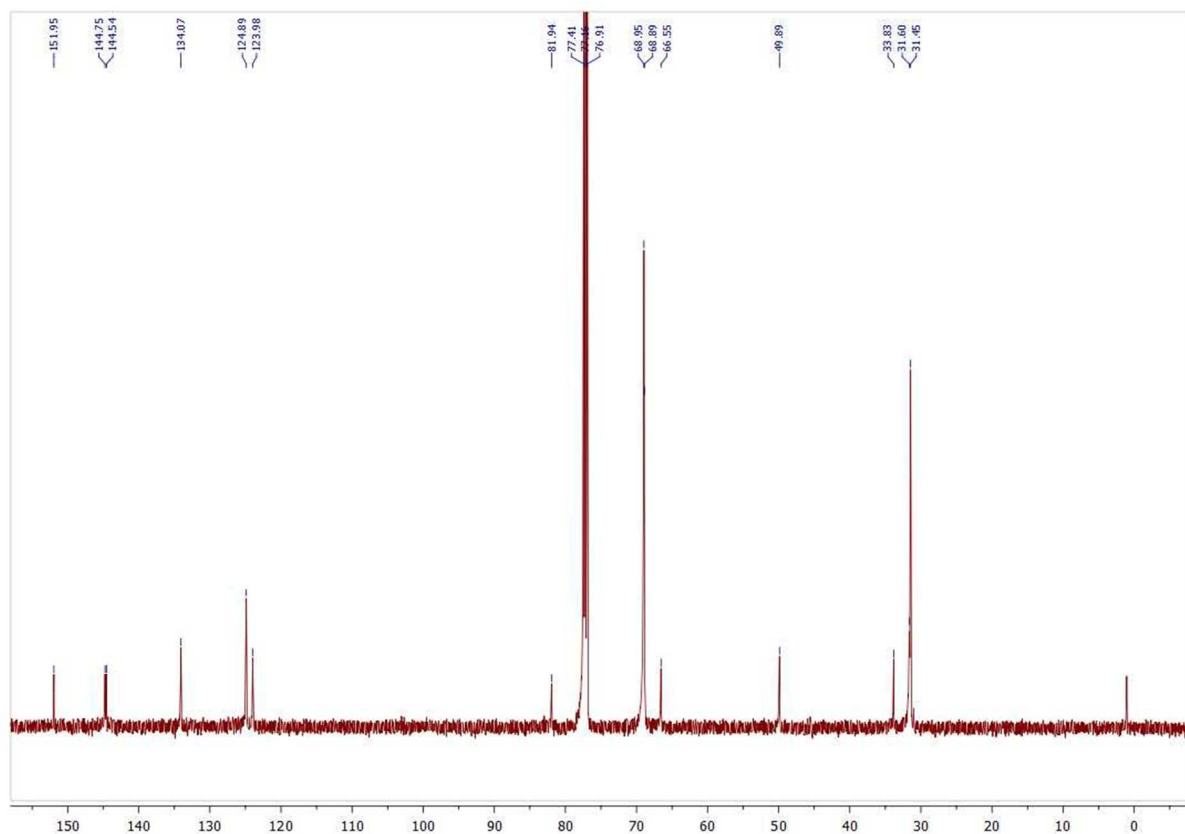


Figure S-30. ^{13}C NMR spectrum of compound **10** in CDCl_3 .

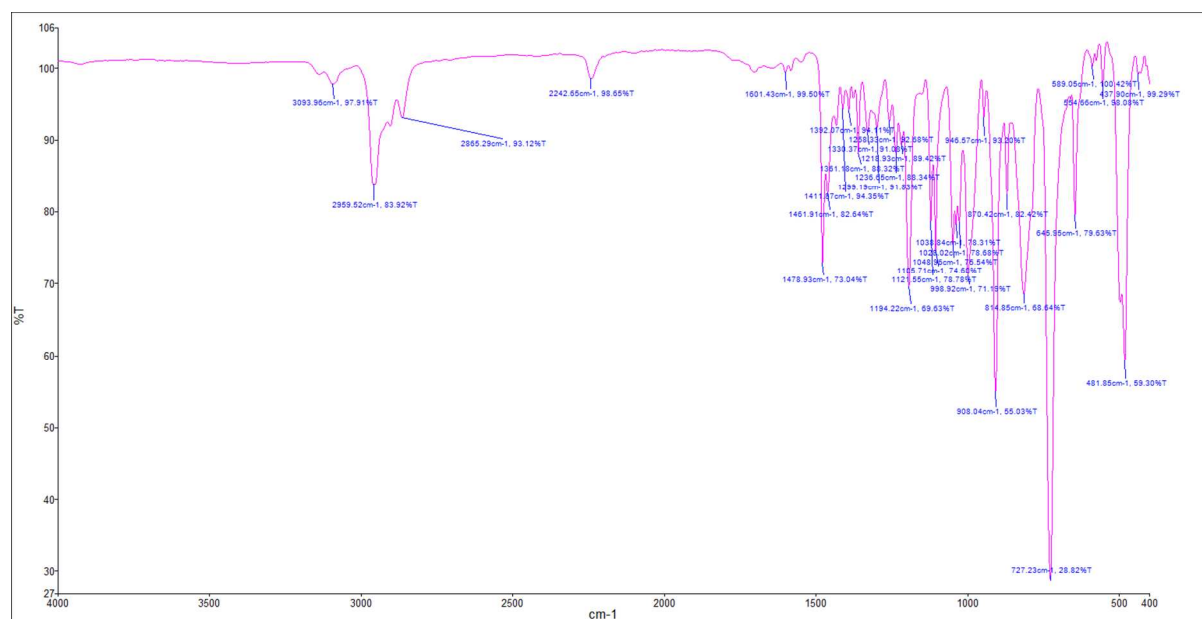


Figure S-31. IR spectrum of compound **10**.

Compound 11

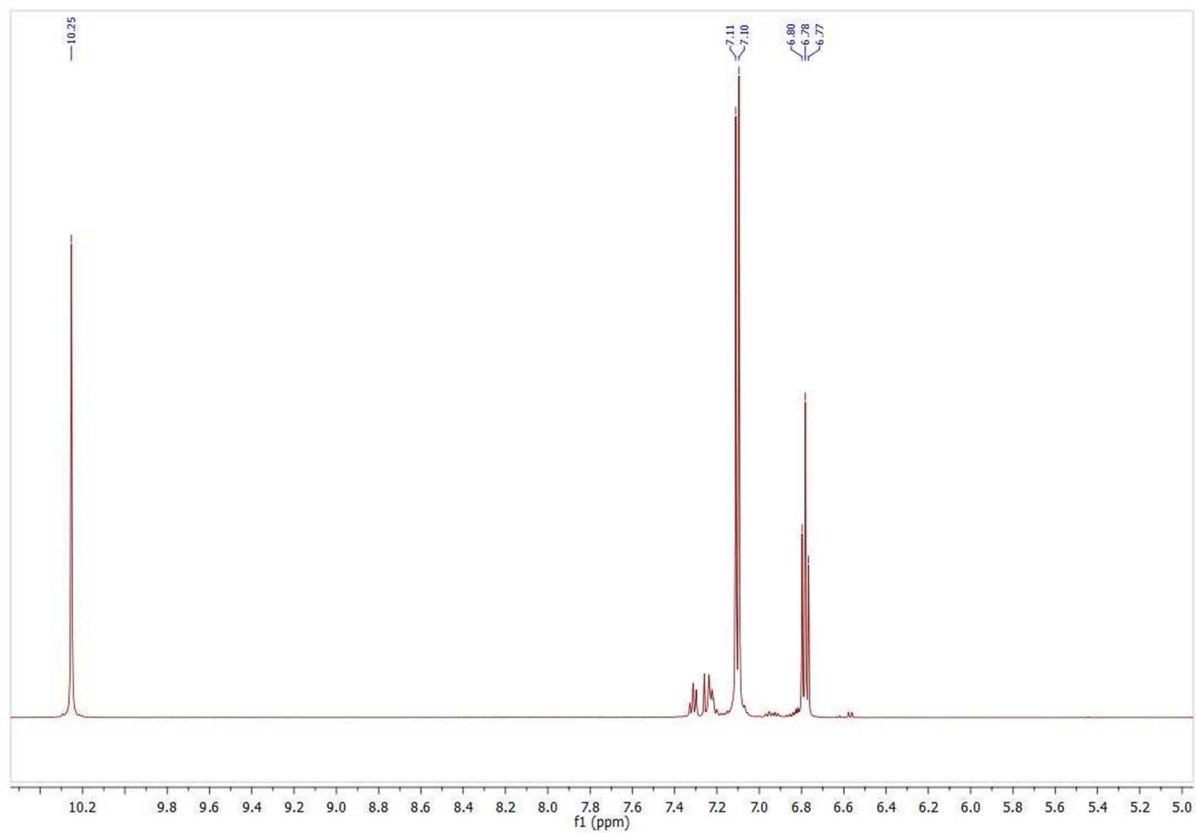


Figure S-32. ^1H NMR spectrum of compound **11** in CDCl_3 .

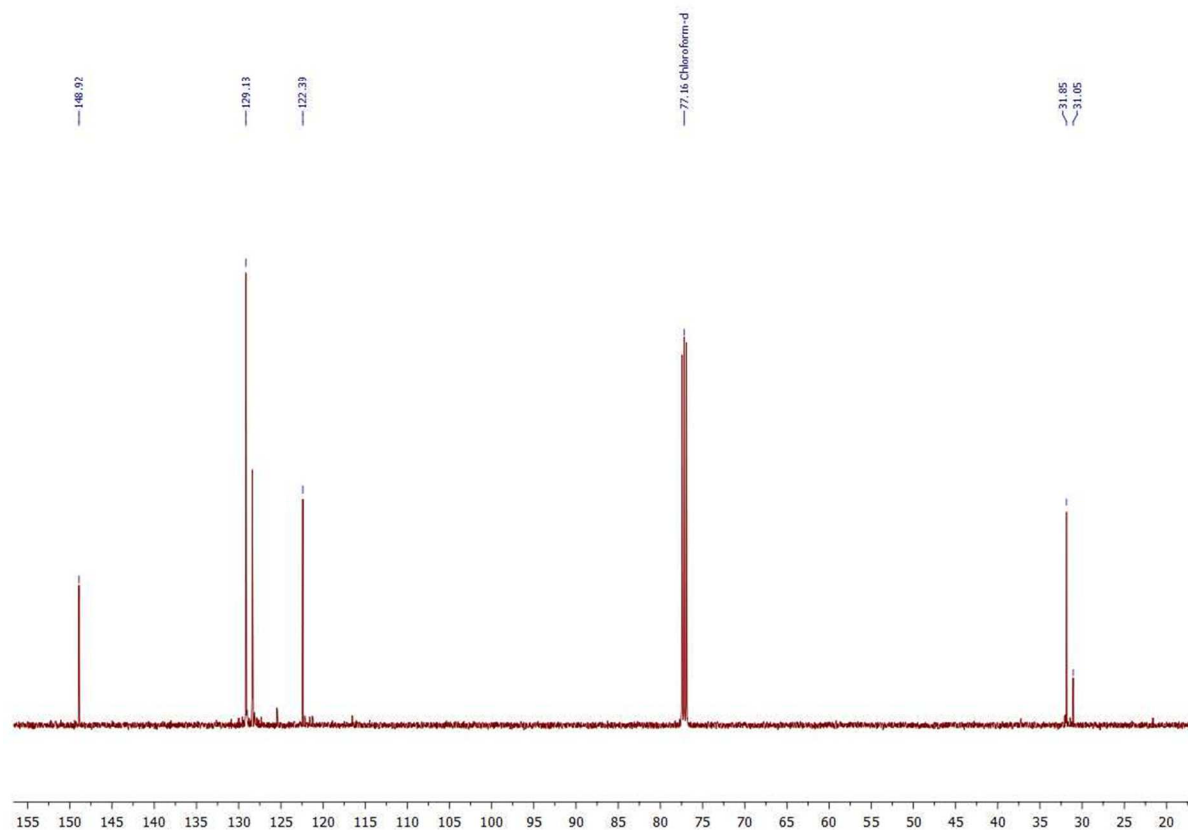


Figure S-33. ^{13}C NMR spectrum of compound **11** in CDCl_3 .

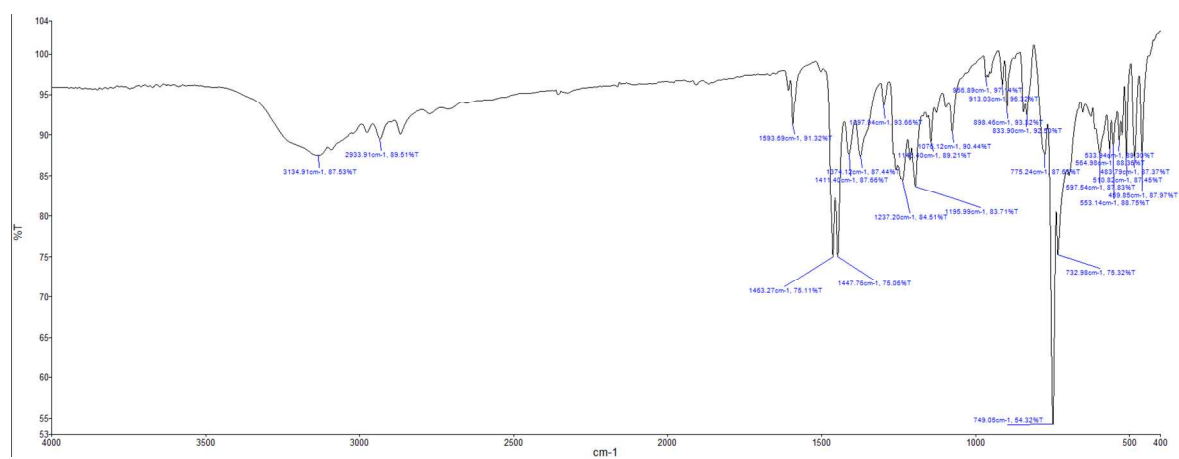


Figure S-34. IR spectrum of compound **11**.

Compound 12

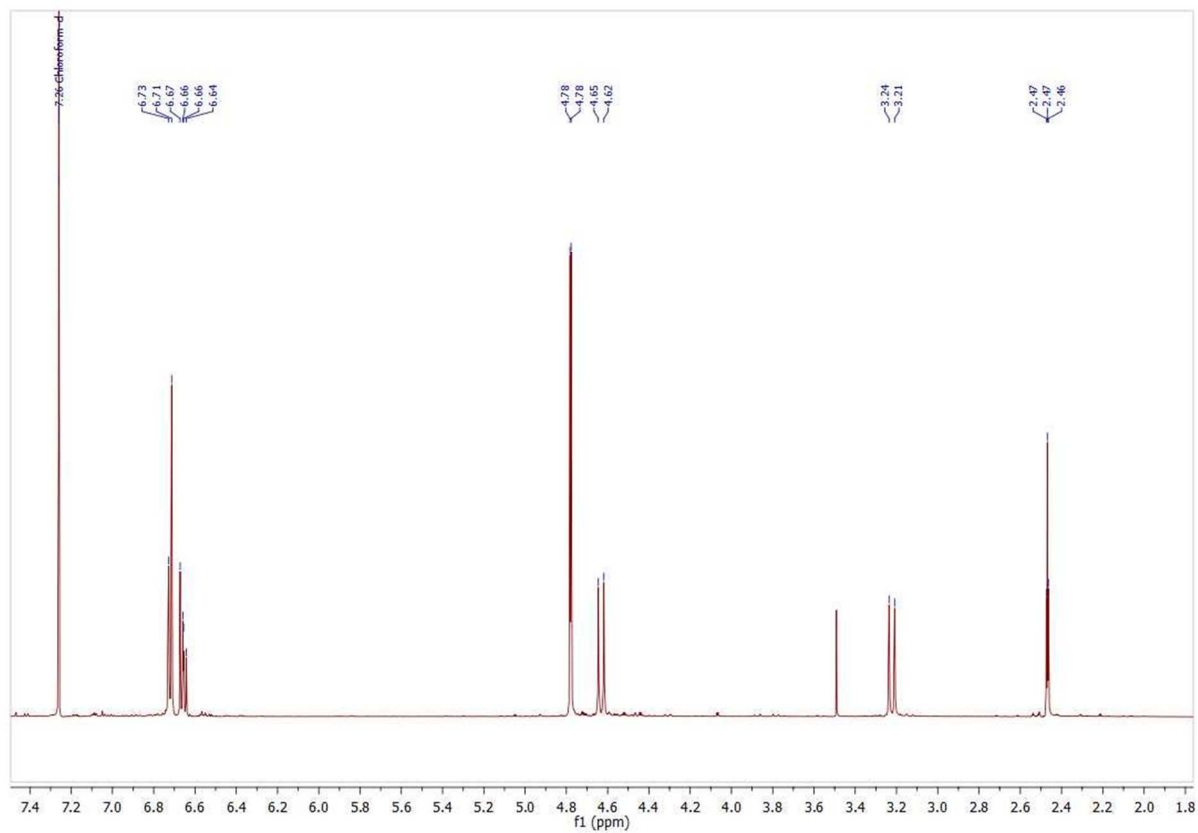


Figure S-35. ^1H NMR spectrum of compound **12** in CDCl_3 .

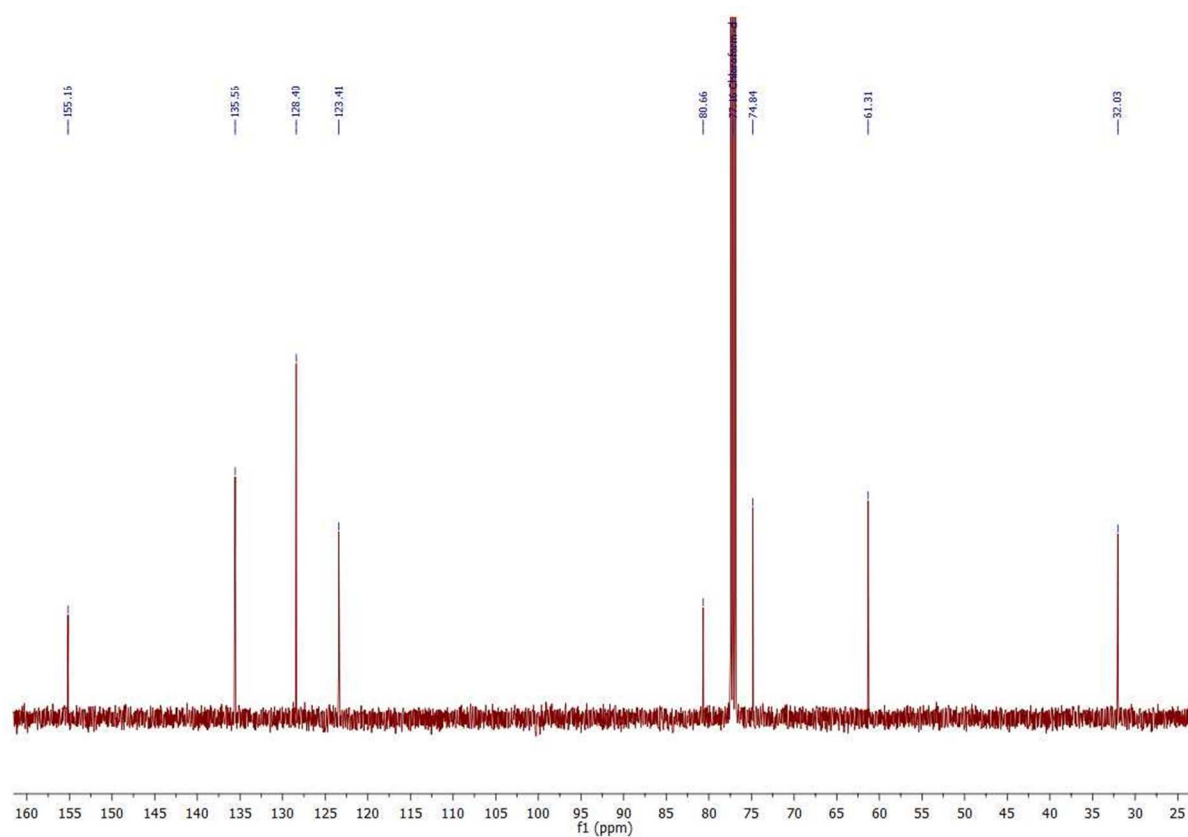


Figure S-36. ¹³C NMR spectrum of compound **12** in CDCl₃.

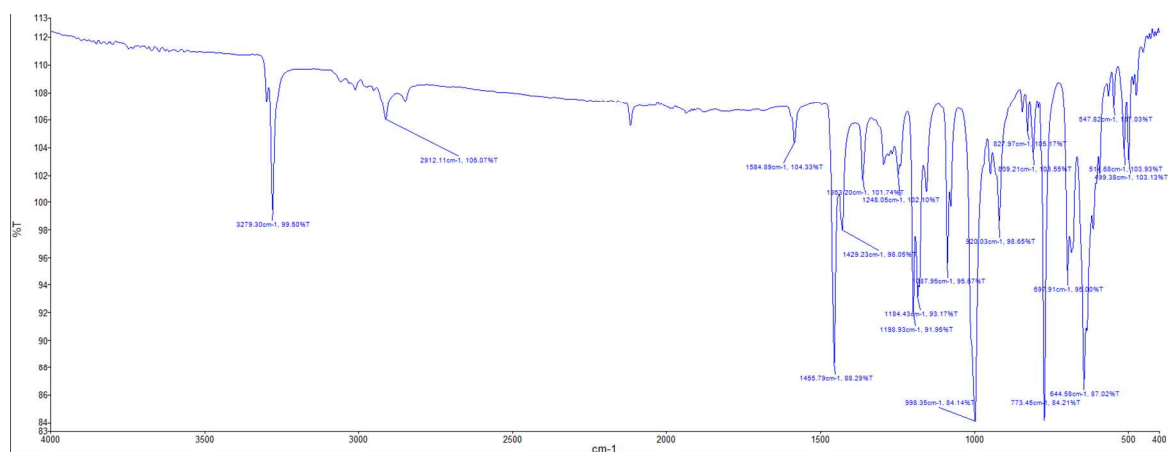


Figure S-37. IR spectrum of compound **12**.

Compound 13

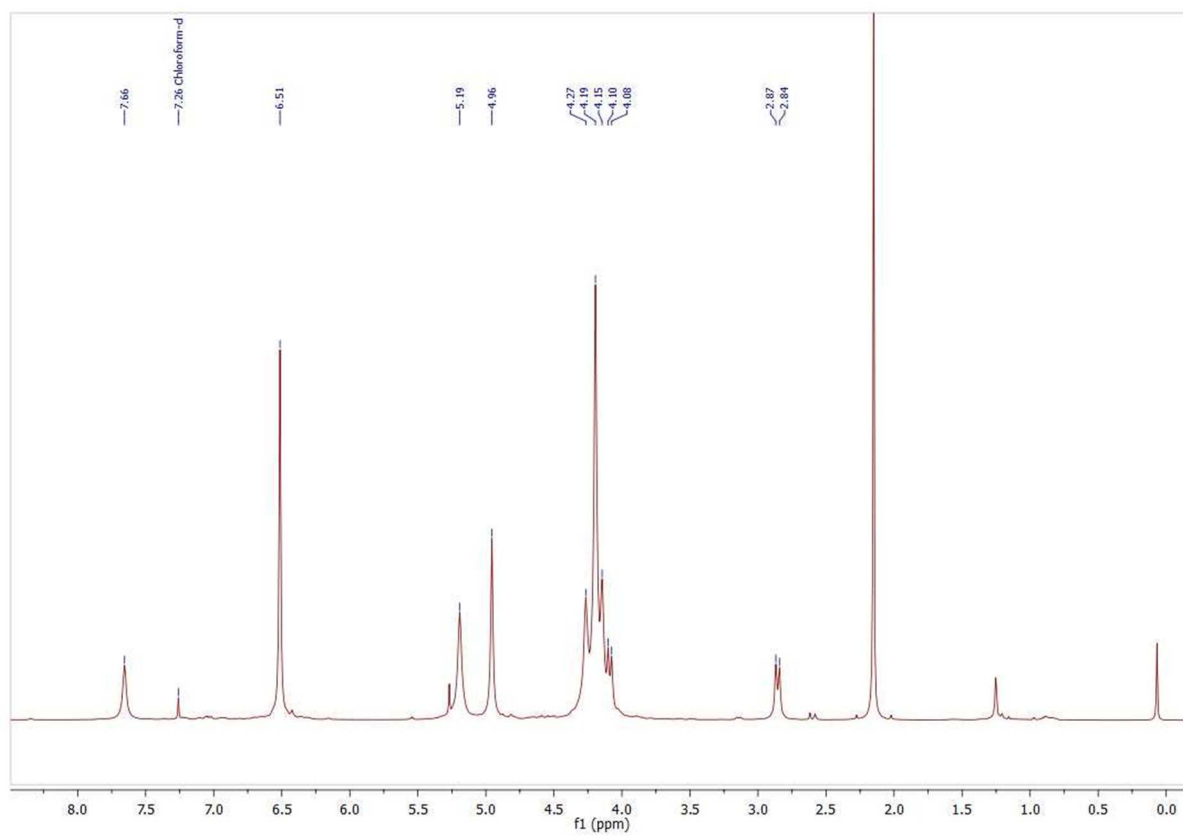
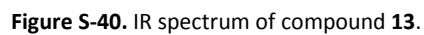
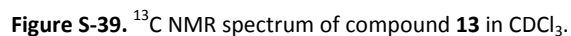


Figure S-38. ^1H NMR spectrum of compound **13** in CDCl_3 .



X-Ray Crystallographic Data for 5 and 9

Single crystals of **5** were grown by slow evaporation of solvents (petroleum ether and acetone); a suitable crystal was selected, encapsulated in a viscous perfluoropolyether and mounted on an Oxford Diffraction Xcaliber-3 single crystal X-ray diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) where the crystal was cooled to 140 K during data collection. The data was reduced and an absorption correction performed using Oxford Diffraction CrysAlisPro.⁶ Using WinGX,⁷ the structure was solved using ShelXS-97, and then refined with ShelXL version 2014/7.^{8,9}

Of the four *O*-alkynyl fragments, one is modeled with a two-component disorder, with 76.5% corresponding to the target *O*-alkynyl fragment; while the remainder is replaced by a simple hydroxyl group and an acetone molecule which occupies the space of the ethyne group. This $-\text{OCH}_2\text{CCH} / -\text{OH}\cdot\text{CH}_3\text{C}(\text{O})\text{CH}_3$ alternative grouping is the only site of disorder in the calixarene molecule. An additional molecule of solvent of crystallization (acetone) was also present in the asymmetric unit, although highly disordered.

The principal component in the crystal examined is the tetra-oxyacetylene product, and this comprises *ca* 76.5% of the sample; in the remainder, one oxyacetylene group is replaced by a simple hydroxyl group and a solvent (acetone) molecule which fills the space of the acetylene group. This $-\text{OCH}_2\text{CCH} / -\text{OH}$ alternative grouping is the only site of disorder in the calixarene molecule.

The calixarene ring shows approximately *mm* symmetry, (Figure S-41). The phenolate rings of O(1) and O(3) are approximately parallel and the normals to these plane are nearly perpendicular (85.2(1) and 80.9(1)°) to the normal to the calixarene ring [defined as the mean-plane of the four bridging CH₂ groups, C(17), C(27), C(37) and C(47)]; the O-CH₂ bonds are directed upwards and outwards from the center of the molecule. The phenolate groups of O(2) and O(4) are tilted 43.6(1) and 38.8(2) ° out of the calixarene ring mean-plane, and are arranged such that the O(2)-CH₂ and O(4)-CH₂ bonds are almost parallel, directed straight upwards from the calixarene plane, with the CH₂ groups in contact across the calixarene ring face. The four acetylene groups point outwards from the centre of the molecule. The nitro groups are essentially coplanar with the adjoining phenyl rings; rotations about the C-N bonds lie in the range 2.3(4) – 12.4(3)°.

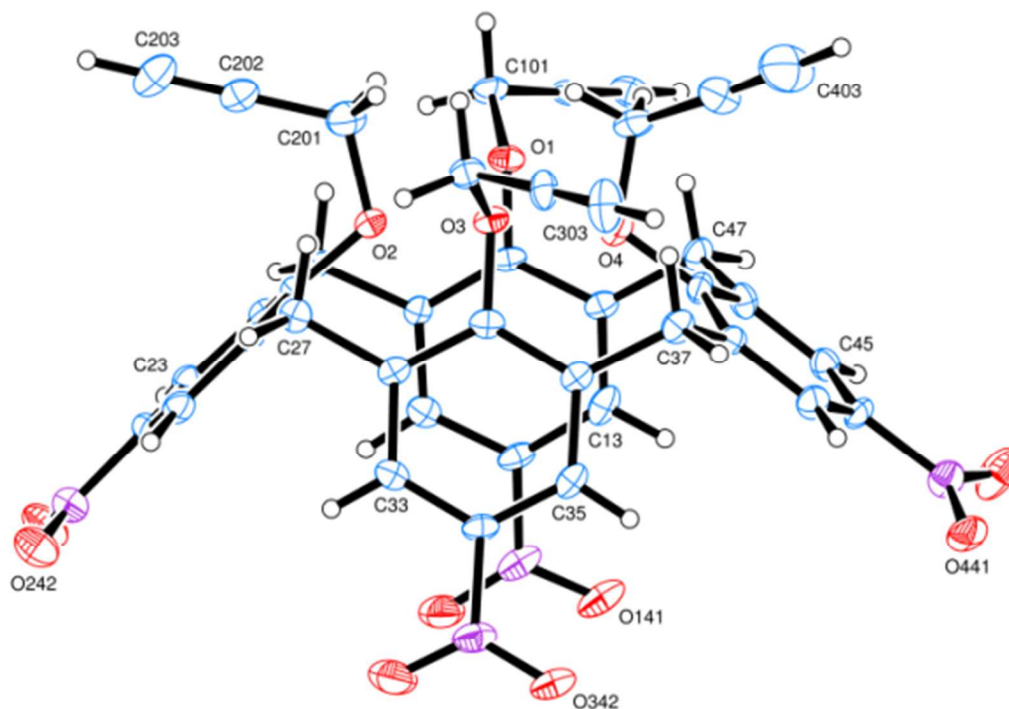


Figure S-41. View of the principal component of compound **5**, indicating the atom numbering scheme (thermal ellipsoids are drawn at the 30% probability level).

In the minor component (Figure S-42), the hydroxyl group, O(4)-H(4), forms a hydrogen bond with O(3); there are no apparent distortions in the rest of the molecule from that of the major component.

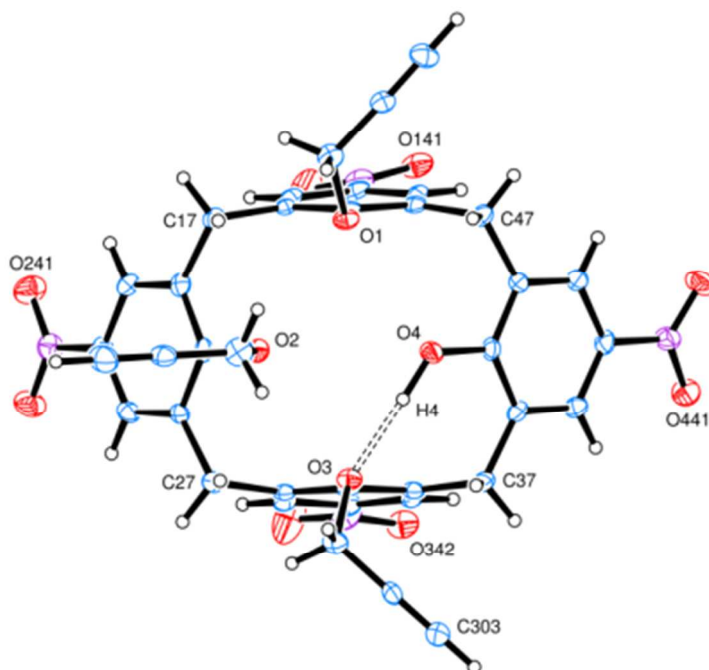


Figure S-42. View of the minor impurity of compound **5**, with the O(4)-H(4) group forming a hydrogen bond with O(3).

Single crystals of **9** were grown from a saturated toluene solution at $-25\text{ }^{\circ}\text{C}$; data collection and processing was performed at the UK National Crystallographic Service at the University of Southampton.¹⁰ Using Olex2,^{11,12} the structure was solved using ShelXS version 2014/7, and then refined with ShelXL version 2014/7.⁹

Of the eight CF_3 fragments, three were modelled with a two-component rotational disorder about the $\text{F}_3\text{C}-\text{C}$ bond, and for four of them it was necessary to model a two-component disorder for the entire $3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3$ fragments related by a *pseudo*-rotation about the phenyl–triazole bond.

Two of the four TBDMS groups exhibit large thermal ellipsoids, indicative of disorder / thermal motion, all attempts to model this was unsuccessful – the largest areas on unassigned electron density were all in vicinity of these groups.

While solvent of crystallization (toluene) was clearly present in the unit cell they were heavily disordered and could not be refined; therefore, using the Olex2 solvent masking function^{11,12} the contribution of the disordered solvent (total electron count comparable to *ca.* 3 toluene molecules in the unit cell) was compensated for (analogous to the SQUEEZE function in PLATON).¹³

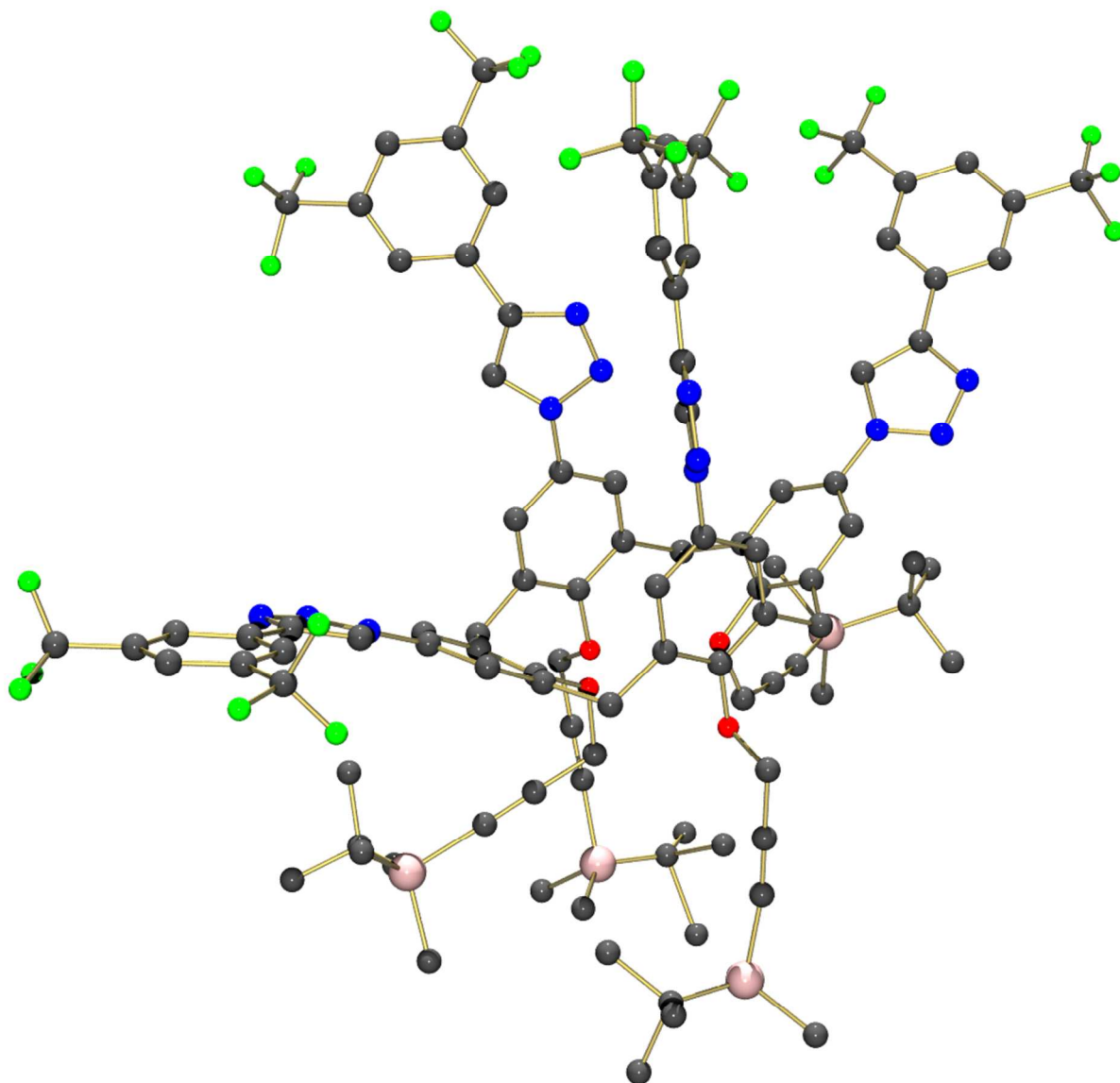


Figure S-43. X-ray crystallographic molecular structure of **9** (hydrogen atoms and minor components of disorder removed for clarity).

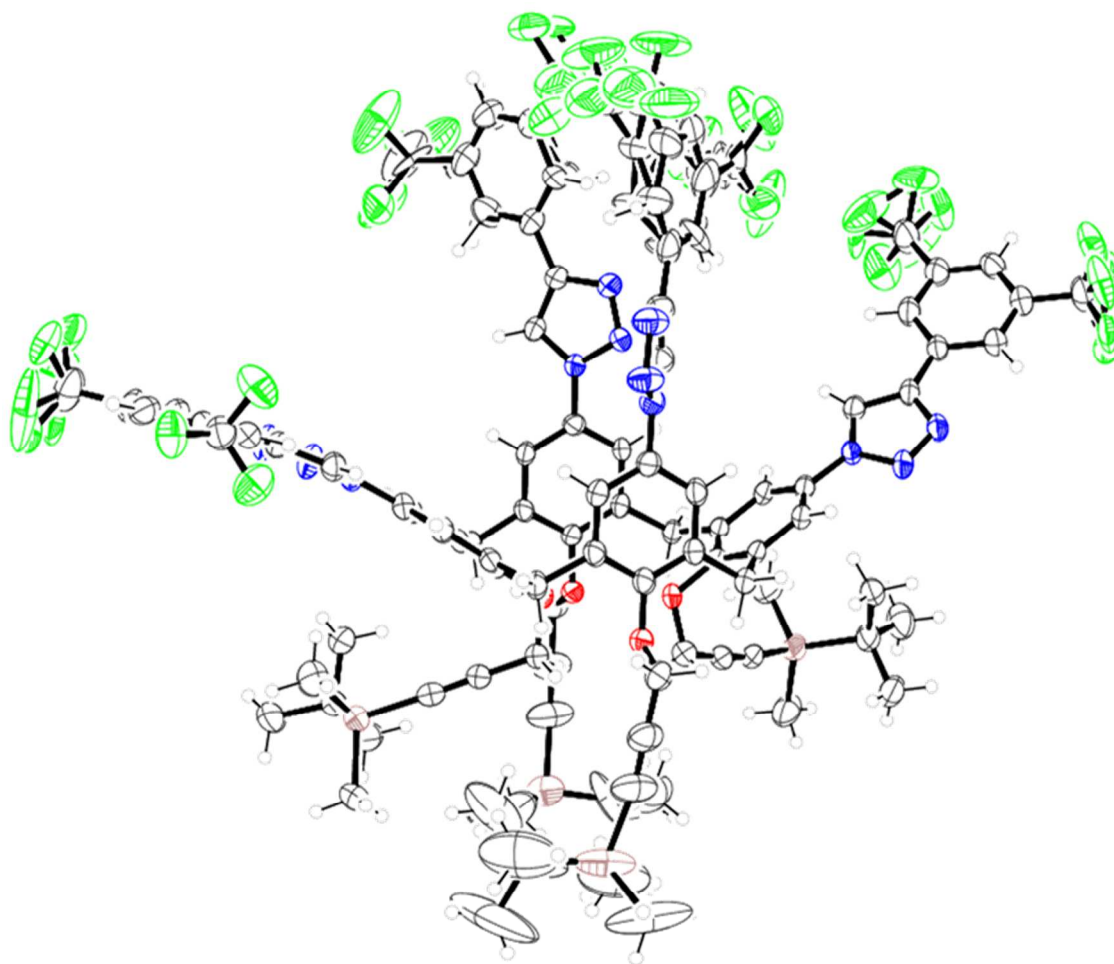


Figure S-44. X-ray crystallographic molecular structure of **9** (thermal ellipsoids are drawn at the 50% probability level).

Table S-1 Crystallographic data for **5** & **9**.

	<i>cone</i> -5,11,17,23-tetra-nitro-25,26,27,28-propargylcalix[4]arene 5·acetone	<i>cone</i> -5,11,17,23-tetra-(4-[3,5-bis(trifluoromethyl)benzene]-1H-1,2,3-triazole-1-yl)-25,26,27,28-TBDMS-propargylcalix[4]arene 9
empirical formula	C ₄₃ H ₃₅ N ₄ O _{13½}	C ₁₀₄ H ₁₀₀ F ₂₄ N ₁₂ O ₄ Si ₄
formula weight	819.75	2150.31
temperature / K	140(1)	100(2)
crystal system	monoclinic	triclinic
space group	P2 ₁ /n	P-1
<i>a</i> / Å	11.5321(6)	12.2448(2)
<i>b</i> / Å	23.8990(14)	21.1239(3)
<i>c</i> / Å	14.6678(8)	23.5984(5)
α / °	90	80.210(2)
β / °	94.030(4)	80.212(2)
γ / °	90	75.892(2)
volume / Å ³	4032.5(4)	5780.6(2)
<i>Z</i>	4	2
ρ_{calc} / mg.mm ⁻³	1.350	1.235
μ / mm ⁻¹	0.102	0.142
F(000)	1708	2224
crystal size / mm ³	0.40 × 0.17 × 0.035	0.126 × 0.063 × 0.038
radiation	Mo K α (λ = 0.71073 Å)	Mo K α (λ = 0.71075 Å)
2 θ range for data collection	5.77 to 43.00°	3.46 to 50.05°
index ranges	-11 ≤ <i>h</i> ≤ 11, -24 ≤ <i>k</i> ≤ 24, -15 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 14, -25 ≤ <i>k</i> ≤ 25, -28 ≤ <i>l</i> ≤ 27
reflections collected	40810	85652
independent reflections	4617 [<i>R</i> _{int} = 0.127, <i>R</i> _{sigma} = 0.0434]	20419 [<i>R</i> _{int} = 0.0489, <i>R</i> _{sigma} = 0.0434]
data / restraints / parameters	4617 / 0 / 589	20419 / 389 / 1644
goodness-of-fit on F ²	1.201	1.063
final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0835, <i>wR</i> ₂ = 0.1291	<i>R</i> ₁ = 0.0931, <i>wR</i> ₂ = 0.2613
final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1139, <i>wR</i> ₂ = 0.1395	<i>R</i> ₁ = 0.1245, <i>wR</i> ₂ = 0.2809
largest diff. peak / hole / e.Å ⁻³	0.23 / -0.27	0.95 / -1.28

CCDC 1477182 (**5**), 1418536 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Surface attachment CVs

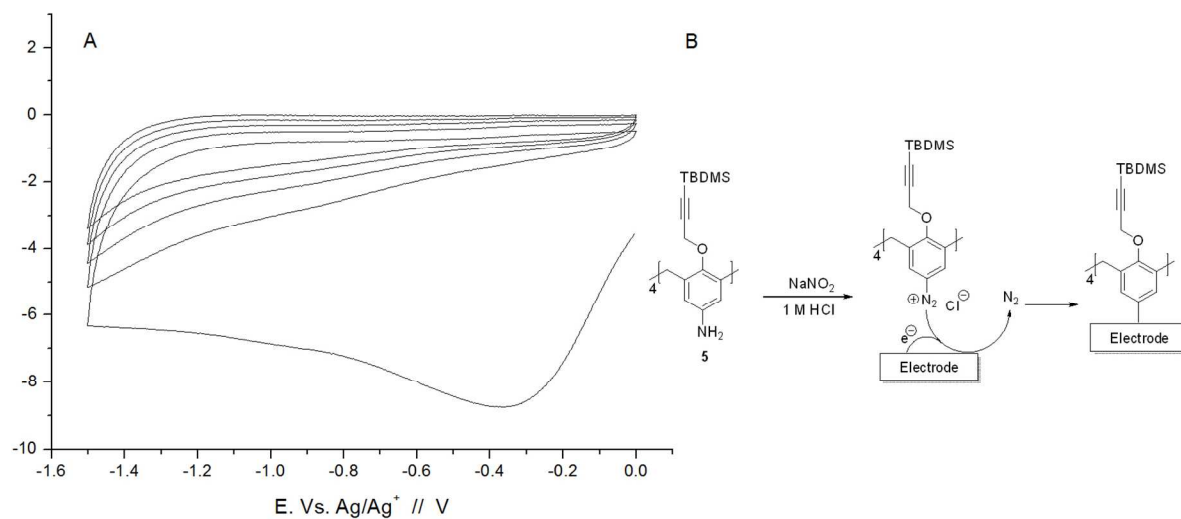


Figure S-45. A. GCE modification with diazonium salt of compound **5** (CH_3CN , 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte). **B.** Shows the formation of the diazonium from calixarene **5** and the subsequent reduction onto the electrode surface.

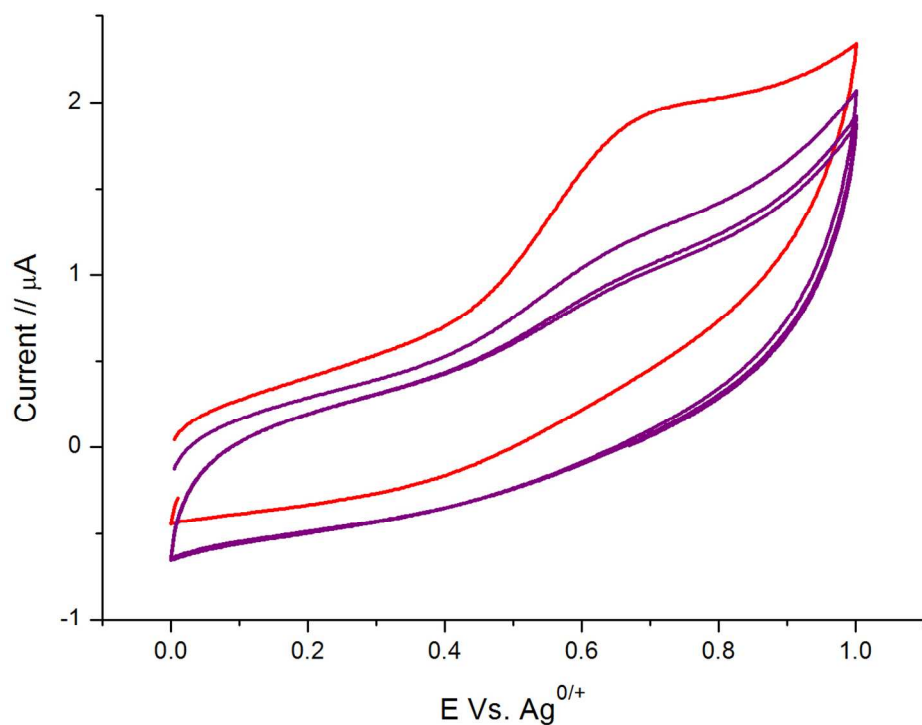


Figure S-46. Oxidation of lithiated calixarene **5** to form the alkynyl radical for surface adsorption (first scan in red).

XPS full survey spectrum

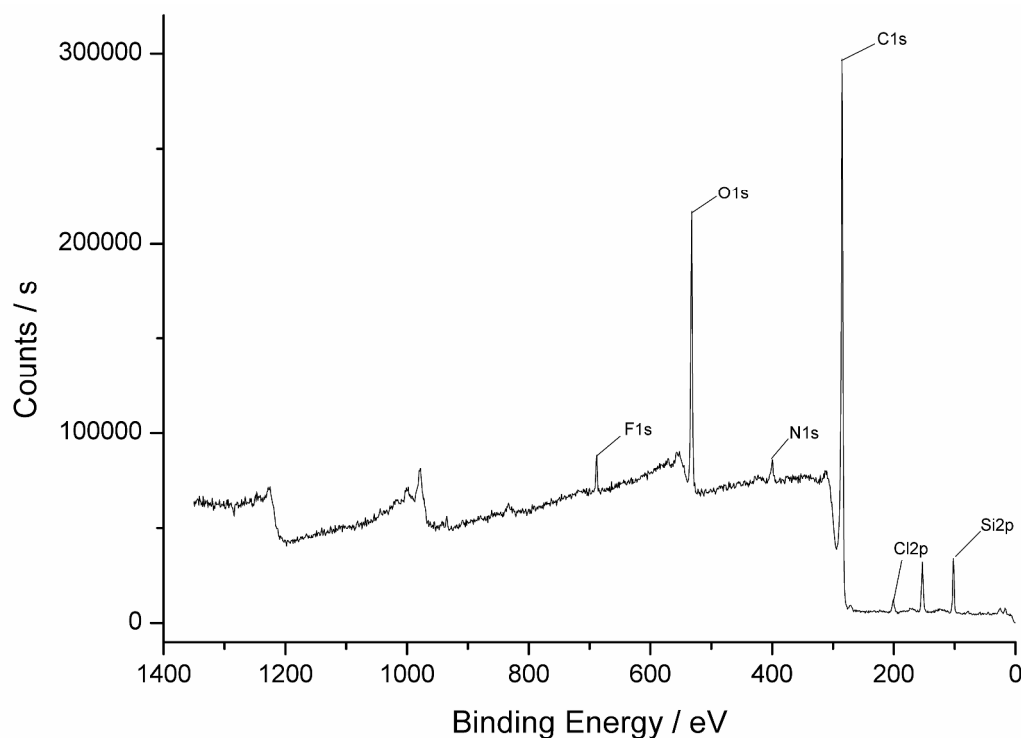


Figure S-47. XPS full survey spectrum of GCE modified with calixarene **8** after post surface functionalization with 1-ethynyl-3,5-bis(trifluoromethyl)benzene.

Data table for figure 5

Scan rate / V s^{-1}	Reductive peak width at half height / V	Oxidative peak width at half height / V	Peak separation / V
0.05	0.33502	0.33421	0.1352
0.1	0.33986	0.37451	0.1878
0.15	0.32912	0.36874	0.1993
0.2	0.3458	0.36819	0.2200
0.25	0.34689	0.39426	0.2284
0.5	0.35258	0.40289	0.2495
0.75	0.39662	0.45075	0.2634

Figure S-488. Data table for figure 5 from manuscript.

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